A DICTIONARY

OF

DYES, MORDANTS, & OTHER COMPOUNDS

USED IN

DYEING AND CALICO PRINTING.

A DICTIONARY

OF

DYES, MORDANTS,

AND OTHER COMPOUNDS

USED IN

DYEING AND CALICO PRINTING.

BY

CHRISTOPHER RAWSON,

F.I.C., F.C.S.,

CONSULTING CHEMIST TO THE BEHAR INDIGO PLANTERS'
ASSOCIATION; CO-AUTHOR OF "A MANUAL
OF DYEING;"

WALTER M. GARDNER,

F.C.S.,

HEAD OF THE DEPARTMENT OF CHEMISTRY AND DYEING,
BRADFORD MUNICIPAL TECHNICAL COLLEGE; EDITOR
OF THE "JOURN. SOC. DYERS AND COLOURISTS;"

AND

W. F. LAYCOCK, Ph.D., F.C.S.

ANALYTICAL AND CONSULTING CHEMIST.

PREFACE.

THIS work has been prepared as a companion volume to *A Manual of Dyeing*, and at the request of the publishers was put into the form of a Dictionary. It comprises a general description of Dyes, Mordants, and Other Substances employed in Dyeing and Calico Printing, with their properties and uses; and, as far as possible, the methods of examining and assaying these various bodies are detailed.

Our chief endeavour has been to produce a book which would be of practical use in the laboratories of Colour Chemists, &c. Methods of applying the Dyes, Mordants, &c., are not given, as these are to be found in the Manual referred to, but in certain other directions there has necessarily been some overlapping between the new and the older work, and we have, with the permission of the authors of the latter, made extracts from that work whenever it seemed desirable to do so.

We have to thank the following gentlemen for permission to use information from the publications mentioned :—

Drs. Schultz and Julius, *Tabellarische Übersicht der Künstlichen organischen Farbstoffe;* Mr. A. G. Green, F.I.C., F.C.S., *Systematic Survey of the Organic Colouring Matters,* and *Tables for the Analysis of Coal-tar Colours;* Mons Leon Lefèvre, *Matières Colorantes Artificielles;* Herr A. G. Rota and the Editor of the "Chemiker Zeitung," *Tables for the Recognition of Coal-tar Dyes;* and Prof. J. J. Hummel, *Tables Representing the Action of Light on Dyes.*

<div align="right">THE AUTHORS.</div>

In the description of the various coal-tar colours given in this work, the names of the firms by whom the particular dye treated of is manufactured is indicated by contractions, to which the following list is an explanatory reference :—

Contraction.	Firm Referred to.
B. or B.A.S.F., . .	Baden Aniline Co., or Badische Anilin und Soda-Fabrik, Ludwigshafen-on-Rhine.
B.A. Co., ...	British Alizarin Co., London.
Ber. or Berlin, . .	Berlin Aniline Co., or Actien-Gesellschaft für Anilin Fabrikation, Berlin.
By. or Bayer, . .	The Bayer Co., or Farbenfabriken vorm. Fr. Bayer & Co., Elberfeld.
B.K., ...	Beyer & Kegel, Leipzig.
Br.S. or Br.S. & S., .	Brook, Simpson & Spiller, Ltd., London.
C. or Cassella, . .	L. Cassella & Co., Frankfurt.
Cl. Co. or Clayton, .	Clayton Aniline Co., Manchester.
C.R., ...	Claus & Rée, Manchester.
D. or Dahl, . .	Dahl & Co., Barmen.
D. & H. or Durand, .	Durand, Huguenin & Co., Basle.
Fi. or Fischesser, .	A. Fischesser & Co., Mulhausen.
G. or Geigy, . .	J. R. Geigy, Basle.
H. or Holliday, .	Read Holliday & Sons, Ltd., Huddersfield.
K. or Kalle, . .	Kalle & Co., Biebrich.
L. or Leonhardt, .	Leonhardt & Co., Mühlheim.
Lev. or Levinstein, .	I. Levinstein & Co., Ltd., Manchester.
M. or M.L. & B., .	Meister, Lucius & Brüning, Höchst.
Mo. or Monnet, .	Gilliard, Monnet & Cartier, Lyons.
O. or Oehler, . .	K. Oehler, Offenbach.
P. or Poirrier, . .	Société Anonyme des Matières Colorantes (A. Poirrier and G. Alsace), St. Denis.
S.C.I. or Bindschædler, .	Society of Chemical Industry (Bindschædler & Busch), Basle.
Sch. or Schollkopf, .	Schollkopf Aniline Co., Buffalo.

A DICTIONARY OF DYESTUFFS.

ACETALDEHYDE *v.* ALDEHYDE.

ACETANILIDE, $C_6H_5.NHC_2H_3O$, *Antifebrin*. On boiling glacial acetic acid and aniline together for some hours the aniline acetate at first formed loses one molecule of water and is transformed into acetanilide, thus—

$$C_6H_5 . NH_2 . CH_3 . COOH =$$
$$C_6H_5 . NH . CH_3 . CO + H_2O.$$
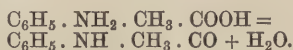
The compound forms white crystals which melt at 112° C., and boil, without decomposition, at 295° C. On boiling with alkalies, the odour of aniline can be detected. Acetanilide is employed in the manufacture of flavaniline.

ACETATES OF ALUMINA *v.* ALUMINIUM ACETATES.

ACETATE OF IRON *v.* IRON (*Ferrous Acetate*).

ACETATE OF LIME *v.* CALCIUM ACETATE.

ACETIC ACID, $C_2H_4O_2$ or $CH_3 . COOH$, *Vinegar, Pyroligneous acid*. Acetic acid occurs in nature in the juices of many plants, either in the free state or in the form of calcium or potassium acetate. It is also produced by the destructive distillation of many organic bodies. The greater portion of that used in commerce is obtained from the distillation products of wood. Acetic acid is also formed by the acetous fermentation of ordinary alcohol and alcoholic liquors—wine, beer, &c. The product is vinegar, which, in addition to acetic acid, contains other organic acids, dextrin, colouring matters, aromatic ethers, &c. Alcohol may be converted into acetic acid by other means than a ferment. Powerful oxidising agents, such as chromic acid, effect the change. In the presence of spongy platinum or platinum black alcohol is converted into acetic acid by the oxygen of the air. The change probably takes place in two stages, aldehyde, CH_3CHO, being formed in the first place, which by further oxidation is converted into acetic acid.

(1) $C_2H_5OH + O = CH_3CHO + H_2O.$
(2) $CH_3CHO + O = CH_3COOH.$
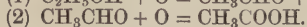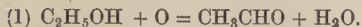
The pure concentrated acid is called *glacial acetic acid* because it solidifies when cooled to 16·7° C., forming an ice-like mass. It is obtained by distilling a *dry* acetate with an equivalent quantity of concentrated sulphuric acid or with a bisulphate.

Pyroligneous acid is the crude acetic acid obtained by the distillation of wood. The aqueous portion of the distillate, separated from the tar, is redistilled; the first portions consist mainly of wood spirit (crude methyl alcohol), and the latter of pyroligneous acid. In addition to acetic acid a great number of other bodies are present, among which are homologues of acetic, crotonic, and angelic acids, furfurol, pyrocatechol, acetone, and other ketones. A purer acid is obtained by neutralising this liquid with lime and decomposing the resulting calcium acetate with sulphuric acid.

Properties.—Pure acetic acid is a colourless body which possesses a strongly acid and pungent smell and taste. It does not redden litmus unless it is diluted with water. It solidifies at 16·7° C. in glistening tabular or prismatic crystals. In a closed vessel the pure acid may, however, be cooled down much below this temperature (even to − 10°) without solidifying, but if disturbed, or if a crystal of the solid acid be dropped in, the whole mass solidifies and the temperature rises to 16·7° C. Acetic acid boils at 118·5° C. and distils without decomposition. The liquid is uninflammable, but the vapour burns with a blue flame, producing water and carbonic acid.

Acetic acid is not oxidised by nitric or chromic acids. Hence it is frequently used as a solvent for organic compounds which are to be subjected to the action of powerful oxidising agents. It is miscible in all proportions with water, alcohol, and ether. The concentrated acid dissolves sulphur, phosphorus, and many organic substances, as well as many metallic salts which are insoluble in water. Acetic acid is a well-defined monobasic acid, but it forms both acid and basic as well as normal salts. All normal acetates are soluble in water. The acid neutralises basic oxides completely, but it does not pre-

1

vent or affect so many chemical processes as the strong inorganic acids and oxalic acid do; further, it does not attack vegetable fibre either in solutions or on drying or in steaming. Hence acetic acid is largely used in dyeing and textile printing. On the addition of water to glacial or concentrated acids heat is liberated and contraction takes place. A mixture containing 77 per cent. of pure acid and 23 per cent. of water corresponds to the hydrate $C_2H_4O_2, H_2O$, and has the highest specific gravity known in mixtures of these substances—viz., 1·075 at 15·5° C. A mixture of about equal parts of acetic acid and water has the same specific gravity as the pure acid. In determining the strength of strong acid by the hydrometer this fact must be taken into account.

Application.—Acetic acid is largely used in the preparation of acetates of calcium, copper, aluminium, iron, chromium, lead, &c., many of which are employed in dyeing and calico printing. In many cases, as, for instance, in the preparation of pyrolignite of iron, the crude pyroligneous acid is used; the empyreumatic substances present in the acid prevent premature oxidation of the iron, and, for this reason, such an "iron liquor" is preferred to one made from purer acetic acid. Acetic acid is largely used as an "assistant" in dyeing and printing, and for neutralising water charged with earthy and alkaline carbonates in dyeing with alizarin and other colouring matters. During the past decade the amount of acetic acid used for these purposes has greatly increased. It is also used in the preparation of colouring matters. Commercial acetic acid is sold of various degrees of strength, the principal strengths containing 25 and 40 per cent. respectively.

Examination and Analysis.—Commercial glacial acetic acid should contain at least 97 per cent. of absolute acid. If 9 volumes of oil of turpentine be agitated with 1 volume of acid, no turbidity will be produced if the acid contain 97 per cent. or upwards. Acid of 99·5 per cent. produces no turbidity with any proportion of turpentine. If a mixture of equal volumes of acid and carbon bisulphide, placed in a dry test-tube and warmed by the hand, becomes turbid, the presence of water is indicated. The strength of weak solutions of pure acetic acid may be conveniently ascertained by means of a good hydrometer. On account of the anomaly, however, regarding the specific gravity of solutions of acetic acid, mentioned above, a direct determination of the density for solutions above 1·055 is of no avail, since the specific gravities above 1·055 correspond to two liquids of different strengths. In order to find whether a certain solution contains more or less than 77 per cent. of acetic acid

(the proportion which yields the highest specific gravity), a little water may be added, and the density taken again. If the specific gravity increases the acid was above 77 per cent.; if otherwise, the mixture was below this strength. With the crude, highly-coloured acid, the specific gravity is, however, no index of the strength whatever.

The following table shows the percentage of acetic acid in solutions of various densities :—

SPECIFIC GRAVITY OF ACETIC ACID AT 15°C.

(Oudeman.)

Specific Gravity.	Per cent. $C_2H_4O_2$.	Specific Gravity.	Per cent. $C_2H_4O_2$.
0·9992	0	1·0623	51
1·0007	1	1·0631	52
1·0022	2	1·0638	53
1·0037	3	1·0646	54
1·0052	4	1·0653	55
1·0067	5	1·0660	56
1·0083	6	1·0666	57
1·0098	7	1·0673	58
1·0113	8	1·0679	59
1·0127	9	1·0685	60
1·0142	10	1·0691	61
1·0157	11	1·0697	62
1·0171	12	1·0702	63
1·0185	13	1 0707	64
1·0200	14	1·0712	65
1·0214	15	1·0717	66
1·0228	16	1·0721	67
1·0242	17	1·0725	68
1·0256	18	1·0729	69
1·0270	19	1·0733	70
1·0284	20	1·0737	71
1·0298	21	1·0740	72
1·0311	22	1·0742	73
1·0324	23	1·0744	74
1·0337	24	1·0746	75
1·0350	25	1·0747	76
1·0363	26	1·0748	77
1·0375	27	1·0748	78
1·0388	28	1·0748	79
1·0400	29	1·0748	80
1·0412	30	1·0747	81
1·0424	31	1·0746	82
1·0436	32	1·0744	83
1·0147	33	1·0742	84
1·0459	34	1·0739	85
1·0470	35	1·0736	86
1·0481	36	1·0731	87
1·0492	37	1·0726	88
1·0502	38	1·0720	89
1·0513	39	1·0713	90
1·0523	40	1·0705	91
1·0533	41	1·0696	92
1·0543	42	1·0686	93
1·0552	43	1·0674	94
1·0562	44	1·0660	95
1·0571	45	1·0644	96
1·0580	46	1·0625	97
1·0589	47	1·0604	98
1·0598	48	1·0580	99
1·0607	49	1·0553	100
1·0615	50		

For a reliable determination of acetic acid, it is necessary to resort to titration with a standard solution of alkali (*v.* ACIDIMETRY).

For this purpose, phenolphthaleïn or Congo red should be used as indicator. The end reaction is sharp, and, even with highly-coloured liquids, if diluted, the termination is usually unmistakable. Litmus, methyl orange, and other indicators are not suitable for acetic acid titration. 25 c.c. of the sample are weighing out and diluted to 500 c.c.; 100 c.c. are withdrawn and titrated, with the addition of a few drops of phenolphthaleïn solution, with normal or semi-normal caustic soda. 1 c.c. of normal caustic soda = ·06 $C_2H_4O_2$.

Example.—25 c.c., weighing 26·08 grms., were diluted to 500 c.c. 100 c.c. with phenolphthaleïn required 35 c.c. normal caustic soda. Then—

$$(\cdot060 \times 35 \times 5 \times 100) \div 26 \cdot 08 = 39 \cdot 80$$
per cent. $C_2H_4O_2$.

In cases where the solution is of a deep brown colour, the following process, recommended by Mohr, may be used :—About 5 grms. of the sample are dissolved, and treated with a known weight of pure dry calcium carbonate, in excess of that required to combine with the acid present. The liquid is boiled and filtered, the residue washed with hot water, and the undissolved calcium carbonate dissolved in a known excess of standard nitric acid, and titrated back with caustic soda.

Example.—5 grms. were treated with 2 grms. of $CaCO_3$, as above. To the residual $CaCO_3$ 30 c.c. of normal nitric acid were added, and it was found that 8·5 c.c. of normal caustic soda were required to neutralise the liquid. Consequently, the residual calcium carbonate neutralised 21·5 c.c. of normal nitric acid = 1·0575 grm. $CaCO_3$. The acetic acid in 5 grms. of sample, therefore, neutralised ·9425 grm. $CaCO_3 = 1 \cdot 131$ grm. $C_2H_4O_2$ (100 $CaCO_3$ = 120 $C_2H_4O_2$), and 1·131 × 100 ÷ 5 = 22·62 per cent. $C_2H_4O_2$.

Impurities.—Commercial acetic acid is liable to contain as impurities and adulterations sulphuric acid and sulphates ; hydrochloric acid and chlorides ; iron, lead, and calcium, as well as empyreumatic bodies.

Sulphuric acid, free or combined, is detected and estimated by precipitation with barium chloride ; *hydrochloric acid*, by silver nitrate ; *calcium salts*, by the addition of ammonium oxalate ; and *iron* and *lead* as in SULPHURIC ACID (*q.v.*).

Total solid matter may be determined by evaporating 20 c.c. to dryness, and heating in the air-bath at 110° C.

Empyreumatic and other *organic bodies*, if present in large quantities, may be at once detected by the colour and smell. Smaller amounts may be detected by neutralising with sodium carbonate, and gently warming the solution. Acetic acid containing these organic bodies darkens in colour when heated with concentrated sulphuric acid. An approximate estimation of the empyreumatic bodies present may be made by diluting 5 or 10 c.c. with 500 c.c. water, adding dilute sulphuric acid, and titrating with decinormal permanganate until the pink colour remains for about a minute.

Free mineral acids may also be detected by moistening strips of white calico with the acid, and drying at 90° to 100°. If hydrochloric or sulphuric acid be present, the fibre is "tendered," disintegrated, or even charred. *Free sulphuric acid* may be detected and estimated by evaporating 10 to 50 c.c. to a syrup, and, when cold, adding strong alcohol. Free sulphuric acid remains in solution, whereas sulphates are precipitated. The liquid is filtered and diluted with water, the alcohol boiled off, and barium chloride added. The barium sulphate is then treated in exactly the same manner as described under *Normal Sulphuric acid v.* ACIDIMETRY.

For the estimation of acetic acid in metallic acetates, see *Calcium acetate.*

ACETIN, $C_3H_5(O \cdot C_2H_3O)_3$, *Triacetin.*

Preparation.—Acetin is produced by heating 82 parts of glacial acetic acid with 60 parts of glycerin for fifteen hours at a temperature of 120° C. in an enamelled vessel. The excess of acetic acid is expelled by increasing the temperature to 160° C. The residual acetin is then syphoned off. About 93 parts of acetin is the usual yield.

Properties.—Acetin, when pure, boils at 259° C. Its specific gravity is 1·155. It is insoluble in carbon bisulphide and petroleum ether, but is miscible with ether, alcohol, chloroform, or benzol. Commercial *acetin* is a thick liquid, the colour of which varies from light to dark brown, according to the quality of the glycerin used. It consists of a mixture of di- and triacetin with smaller amounts of glycerin and water. The liquid smells of acetic acid. The density varies from 32° to 38° Tw. The higher the specific gravity the less free acetic acid is present.

Acetin is employed as a solvent for basic colouring matters—*e.g.*, induline, Perkin's violet, &c. Acetin is preferable to ethyl- and methyl-tartaric acids (which are used for the same purpose), because it injures the fibres less than tartaric acid. Both tartaric acids mentioned are valued in a similar manner to acetin—viz., by estimating the free and combined tartaric acid.

Analysis.—Kopp and Grandmougin * recommend the method mentioned below. The greater the amount of combined acid present the more valuable the sample.

Free Acid.—50 grms. of acetin are diluted with water to 500 c.c. In 50 c.c. of this

* *Bull. Soc. Ind. Mulhouse,* 1894, pp. 112 - 116
Journ. Soc. Chem. Ind., 1894, p. 720.

solution the free acetic acid is determined by means of phenolphthaleïn and normal caustic soda.

Example.—50 c.c. (5 grms.) require 5 c.c. $\frac{N}{1}$ NaOH. 1 c.c. $\frac{N}{1}$ NaOH = 0·06 grm. acetic acid—*i.e.*, 5 c.c. $\frac{N}{1}$ NaOH = 0·30; and $\frac{0·30 \times 100}{5}$ = 6 per cent. free acetic acid.

Combined Acid.—10 c.c. (1 grm.) of the acetin solution (made as above) are treated with 15 c.c. of soda, heated to boiling, and boiled for five minutes. After diluting, the excess of soda is determined by normal acid.

Example.—4 c.c. $\frac{N}{1}$ acid were required; then 15 − 4 − 1 of $\frac{N}{1}$ caustic soda (1 c.c. being the amount of $\frac{N}{1}$ alkali required to neutralise the free acid in 10 c.c.) = 10 c.c. $\frac{N}{1}$ NaOH. 1 c.c. $\frac{N}{1}$ NaOH = 0·06 grm. acetic acid—*i.e.*, 10 c.c. $\frac{N}{1}$ NaOH = 0·60, and 0·60 × 100 = 60 per cent. combined acetic acid.

The following table gives results of the analysis of three samples :—

No.	Density.	Acid Free.	Acid Combined	Remarks.
		per ct.	per ct.	
I.	1·1774	9·2	46·0	Acetin obtained with above proportions of glycerol and acetic acid.
II.	1·1896	6·98	55·7	Do. do.
III.	1·1608	23·0	43·5	Almost colourless; smells very strongly of acetic acid.

Sample II. is good ; I. is medium quality ; III. contains too much free, and too little combined, acetic acid.

ACETIN BLUE (B.) *v.* INDULINE.
ACETINDULINE R (M.) *v.* INDULINE.

ACETONE, $C_3H_6O = \frac{CH_3}{CH_3} {>} CO$.

Preparation.—Acetone is obtained by heating a mixture of calcium acetate with excess of calcium hydroxide. O. Porsch * heats the mixture in a vessel surrounded by molten lead, thus obviating overheating. After about 12 per cent. of the acetone has passed over, superheated steam is passed into the mixture to facilitate the reaction.

$$\frac{CH_3 . COO}{CH_3 . COO} {>} Ca = C_3H_6O + CaCO_3.$$
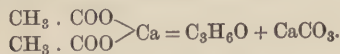
* Eng. Patent, No. 5255, March 12, 1895.

Any tar formed is separated from the liquid, and the crude acetone submitted to fractional distillation. The yield of pure acetone is 25 per cent. from commercial calcium acetate. Acetone is also manufactured from the products obtained by the destructive distillation of wood. The acetone is separated from the other constituents of the distillate after separation of the acetic acid. It can be purified by shaking the mixture containing it with sodium bisulphite, a substance with which it forms a crystalline compound. The crystals are then distilled with sodium carbonate solution when acetone passes over mixed with water. The aqueous distillate is saturated with calcium chloride, and the acetone which forms the supernatant stratum separated and distilled. Acetone is also formed when the vapour of acetic acid is passed through hot tubes.

Properties.—Acetone is a colourless mobile liquid having a peculiar ethereal odour. It boils at 56·5° C. Acetone is a dimethyl ketone, and possesses neither acid nor alcoholic properties. It is miscible with water, alcohol, and ether in all proportions. When an aqueous solution of acetone is treated with caustic potash and iodine solution, iodoform is produced. If alcohol be present, ammonia should be substituted for potash. H. Trimble recommends acetone as the best solvent for the preparation of tannins from oak bark. Acetone is an excellent medium for dissolving many oils and fats.

Analysis.—Acetone should be perfectly clear and limpid, and miscible with water in all proportions, while the mixture should not show any cloudiness, even after long standing. E. R. Squibb * describes the following process modified by Robineau and Rollin, which can be used for determining acetone in the presence of ethyl alcohol. The solutions required are :—(1) *Standard acetone* containing 1 grm. acetone in 100 c.c. ; this solution should be kept in a dark glass bottle. (2) *Potassium iodide* solution prepared by dissolving 250 grms. of the salt in 1 litre of water, and adding 850 c.c. of sodium hydrate solution containing 257 grms. per litre. (3) *Sodium hypochlorite* containing about 2·6 per cent. of available chlorine, and to each litre of which is added 25 c.c. of sodium hydrate solution, 257 grms. per litre. (4) *Starch solution,* 0·125 grm. starch is mixed with 5 c.c. of cold water, and then added to 20 c.c. of boiling water and boiled ; when cold, 2 grms. of sodium bicarbonate are added and dissolved with stirring.

Method of Titration.—10 c.c. of the standard acetone solution and 20 c.c. of the alkaline iodide solution are added together and well stirred. The hypochlorite is added from a

* *Journ. Amer. Chem. Soc.,* 1896, vol. xviii., p. 1068 ; *Journ. Chem. Soc. Ind.,* 1897, p. 168.

burette, iodoform being precipitated, and the end of the reaction is indicated by a blue colour being given with starch. The hypochlorite equivalent of 0·1 grm. of acetone is thus found, and from this the percentage of acetone in a solution of unknown strength can be rapidly estimated. For this purpose from 0·1 to 0·4 c.c. of the solution should be taken, according to its approximate strength. This is weighed, diluted, and titrated as above. Since the hypochlorite solution diminishes in strength on keeping, it should be frequently checked by means of the standard acetone solution.

ACID ALIZARIN BLUE B B (M.). An anthracene derivative. *Sodium salt of hexaoxyanthraquinone disulphonic acid,*

$$C_{14}O_2(OH)_6(SO_3Na)_2$$
$$(OH = 1:2:4:5:6:8, SO_3Na = 3:7).$$
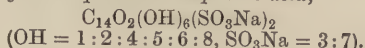
Red-brown crystalline powder, soluble in water, with a red colour; in alkali, with a violet-blue colour; and in concentrated sulphuric acid, with a blue colour. Insoluble in alcohol.

Application.—An acid mordant dye. Dyes *wool* dark blue, the colour being applied with addition of sulphuric acid and Glauber's salt, and subsequently saddened with fluoride of chromium. Not applicable to *cotton.*

ACID ALIZARIN BLUE G R (M.). Constitution, reactions, and application similar to above. Dyes somewhat greener and duller shades than B B.

ACID ALIZARIN BROWN B (M.). 1899. An acid mordant dye, producing very fast brown shades on wool. The colour is dyed in an acid bath, and subsequently saddened with bichromate of potash.

ACID ALIZARIN GREEN B (M.). An anthracene derivative. *Sodium salt of disulphydrotetroxyanthraquinone disulphonic acid,*

$$C_{14}O_2(OH)_4(SH)_2(SO_3Na)_2$$
$$(OH = 1:3:5:7. SH = 4:8. SO_3Na = 2:6).$$
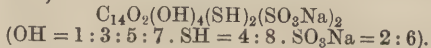
A dark green crystalline powder, soluble in water, with a blue-green colour. Insoluble in alcohol. Alkaline solution, violet. Soluble in concentrated H_2SO_4 with blue-red fluorescent solution.

Application.—Dyed as acid alizarin blue, producing bluish-green shades.

ACID ALIZARIN GREEN G (M.). Constitution, reactions, and application similar to above.

Application.—As above, but dyes somewhat greener shades.

ACID BLACK B and B B (H.). 1890. Azo colours. Bronzy-black crystalline powders. Aqueous solution, violet. In concentrated H_2SO_4 (B), olive-green; (B B), greyish-green. Insoluble in alkali.

Application.—Acid colours. Dye *wool* and *silk* violet-black in acid bath.

ACID BLACK S (H.). Black powder. Aqueous solution bluish-violet, easily soluble. Alcoholic solution greenish-blue, easily soluble. Concentrated H_2SO_4, olive-green; on dilution changes to greenish-blue and then violet.

Application.—An acid colour. Dyes *wool* and *silk* black in acid bath.

ACID BLUE 6 G (C.) *v.* CYANOL EXTRA (C.).

ACID BROWN (D.). *Acid brown* (*P.*). *Fast brown G* (*ter Meer*). A disazo compound.

$$\left.\begin{array}{l}Sulphanilic\ acid\\ Sulphanilic\ acid\end{array}\right\rangle Alpha\ naphthol.$$

Brown powder. Aqueous solution red-brown. Alkaline solution cherry-red. Concentrated H_2SO_4, violet; on dilution brownish-yellow.

Application.—An acid colour. Dyes *wool* and *silk* brown in acid bath.

ACID BROWN (P.) *v.* ACID BROWN (D.).

ACID BROWN G (Ber.). 1882. A disazo compound.

$$\left.\begin{array}{l}Aniline\\ Sulphanilic\ acid\end{array}\right\rangle Phenylene\ diamine.$$

Brown powder. Aqueous solution brown. Alkaline solution brown. Concentrated H_2SO_4, reddish-brown; on dilution yellowish-brown.

Application.—An acid colour. Dyes *wool* and *silk* in acid bath yellowish-brown.

ACID BROWN R (Ber.). 1882. An azo compound.

Naphthionic acid—Chrysoidine.

Brown powder. Aqueous solution brown. Alkaline solution brown. Concentrated H_2SO_4, olive-green; brown ppt. on dilution.

Application.—An acid colour. Dyes *wool* and *silk* reddish-brown in acid bath.

ACID CARMOISINE B (B K) *v.* FAST RED E (B).

ACID CERISE (M). An impure acid magenta.

ACID COLOURS. This term is applied to colouring matters which are employed in an acid bath. The acid colours may be subdivided into the following groups:—

(1) *Sulphonated Basic Colours.*—The members of this group are produced by the introduction of sulpho groups (SO_3H) into colour bases, *e.g.*—

$$\underset{\text{Rosaniline (magenta base).}}{C_{20}H_{14}(OH)(NH_2)_3} \longrightarrow$$

$$\underset{\text{Acid magenta.}}{C_{20}H_{11}(SO_3H)_3(OH)(NH_2)_3}$$
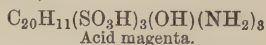
Acid colours of this type are sold as sodium salts—*i.e.*, they contain (SO_3Na) and not (SO_3H) groups. They usually produce similar colours to the basic dyes from which they are derived, but have only from $\frac{1}{2}$ to $\frac{1}{3}$ of their colouring power. They are usually, but not exclusively, derivatives of *triphenyl*

methane, and consist mainly of *green*, *blue*, and *violet* dyes, but also include ACID MAGENTA and AZO CARMINE (two red dyes), and QUINOLINE YELLOW.

AZO CARMINE, QUINOLINE YELLOW, THIOCARMINE (blue), and the soluble INDULINES are not derived from triphenyl methane.

(2) *Azo Sulphonic Acids.*—This group of acid dyes forms, numerically, the largest class of coal-tar colours. It includes the greater proportion of the acid *reds*, *oranges*, *yellows*, *browns*, and *blacks*, and a much smaller number of *greens*, *blues*, and *violets*.

A typical example of a dye belonging to this group is *amidoazo benzene disulphonate of soda* (*acid yellow*) :—

$$C_6H_4 \overset{\text{SO}_3\text{Na}}{\underset{\text{N} = \text{N} - C_6H_3}{\diagdown}} \overset{\text{SO}_3\text{Na}}{\underset{\text{NH}_2}{\diagup}}$$
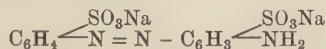
The group is subdivided according to the number and position of the azo groups contained into—

    (*a*) Monazo dyes.
    (*b*) Primary disazo dyes.
    (*c*) Secondary disazo dyes.
    (*d*) Trisazo dyes.
    (*e*) Tetrazo dyes.

The *direct cotton colours*, by constitution, belong for the most part to the group of *azo sulphonic acids*, but their mode of application differs from that of the acid dyes.

(3) *Nitro Compounds.*—This group of acid colours is not numerous, and includes yellow dyes only, of which the most important are PICRIC ACID and NAPHTHOL YELLOW S.

Application.—Generally speaking, the acid dyes are applied to *wool* by boiling the material in a solution of the colouring matter, to which sulphuric acid and sodium sulphate have been added. Modifications of this simple process are, however, frequently necessary to meet special requirements and to secure level colours, &c. For details reference must be made to manuals of dyeing. Acid dyes are applied to *silk* in a slightly acid bath, frequently with addition of "boiled-off" liquor or soap. In *cotton dyeing* these dyes are now rarely used.

LIST OF ACID COLOURS (for Names of Makers see Alphabetical Description of Dyes).

Acid Reds.

Acid Magenta S.
  ,,   Mauve.
  ,,   Ponceau.
  ,,   Rosamine A.
Alkali Fast Red B, R.
  ,,   Red.
Amaranth.
  ,,   extra.
Anisoline.
Anthracene Red.
Apollo Red.
Azo Acid Carmine B.
  ,,   ,,   Magenta G.
  ,,   Bordeaux.
  ,,   Cardinal G.
  ,,   Carmine B X powder.
  ,,   ,,   G paste.
  ,,   Coccine 2 R.
  ,,   Cochineal.
  ,,   Fuchsine B, G, G N extra, S.
  ,,   Eosine.
  ,,   Grenadine L, S.
  ,,   Orchil R.
  ,,   Rubin S.
Bordeaux B extra, G.
Biebrich Scarlet R.
Brilliant Bordeaux S.
    ,,   Croceïne 9 B, 3 B, R.
    ,,   Cochineal M O O.
    ,,   Double Scarlet 3 R.
    ,,   Orchil.

Brilliant Ponceau 5 R.
    ,,   Scarlet R, 2 R, 3 R, 4 R, 6 R, G.
Carmoisine B.
Caroubier.
Cerasine.
Chromazone Red.
Chromotrope 2 B, 4 B, 6 B, 8 B, 10 B, F B, 2 R, S, S B, S R.
Clayton Cloth Red.
Cloth Red B.
Cloth Red G, G extra, 3 G extra, O B, O G, B A, G A, 3 G A.
Cloth Scarlet G paste, R paste.
Coccinine.
Coccine 2 B.
Cochineal Red A, 3 R.
    ,,   Scarlet P S.
Croceïne A Z.
Cresol Red.
Croceïne Scarlet O O, O X, R, B, 3 B, 3 B X, 5 B, 7 B, 10 B.
Crystal Scarlet 6 R.
Cyanosine (spirit soluble).
Double Brilliant Scarlet, 2 R, G.
    ,,   Ponceau 4 R, 3 R, 2 R, 1 R.
    ,,   Scarlet 3 R.
Emin Red.

Eosamine B.
Eosine (yellow shade).
  ,,   extra (crystals).
  ,,   3 G, A, extra spirit soluble.
Erythrine P.
Erythrosines B, B A, 2 R, 1 N.
Fast Acid Eosine G.
  ,,   ,,   Magenta B.
  ,,   ,,   Red A.
  ,,   Claret Red O.
  ,,   Red A, B, D, E, extra, B T, G S, N S.
  ,,   Red P R extra.
  ,,   Scarlet O, B.
Grenadine S B.
Grenat paste.
Guinea Red 4 R.
Jute Scarlet 3 B H, 3 B extra.
Lanafuchsine S B, S G.
Mandarin G extra, G R.
Mars Red G.
Metanil Yellow.
Methyl Eosine.
Milling Red R.
  ,,   Scarlet.
Naphthol Scarlet 3 R.
  ,,   Red S.
New Coccine.
  ,,   Red E.
  ,,   Scarlet 2 G powder, 2 R.
Oënanthine.
Orcelline.

Orchil Red.
  ,,   Substitute 3 V N paste,
      N powder.
Orseilline 2 B.
Palatine Red A.
  ,,   Scarlet A, 3 R.
Phloxine, 2 B.
Ponceau S for silk, 4 G B, R,
  1 R, 2 R, II R, 3 R, 3 R B,
  4 R, 4 RB, 6 R, 6 RB, 10 RB,
  G, BO extra, S extra, 2S.
Pyrotine Red.
Rock Scarlet.
Rosazine.
Rose Bengale B, N T.
Rosinduline B, 2 B, G, 2 G.
Roxamine M.
Safrosine.
Scarlet 2 G, G, R, 2 R, 3 R,
  4 R, 5 R, 6 R, S extra, 2S.
Silk Scarlet G.
Sorbine Red.
Triphenyl Rosaniline.
Tolan Red G.
Vat Red paste.
Wool Scarlet 3 R.

Acid Oranges.

Aniline Orange.
Aurantia.
Croceïn Orange E N.
Gold Orange.
Milling Orange.
Orange N, I, 2, 3, 2G, G, GS,
  GT, extra, T, 2Y, IV, R,
  E N Z.

Acid Yellows.

Acid Yellow.
Alkali Yellow.
Alpine Blue.
Aniline Yellow.
Azo Acid Yellow.
  ,, Flavine.
  ,, Yellow conc.
  ,, Yellow F.
Brilliant Yellow S.
Chrysoïne G.
Cinereïne N
Citranine A.
Curcumeïne extra.
Fast Yellow I, S, extra.
Flavaniline.
Indian Yellow G R.
Martins Yellow.
Metanil Yellow extra, M N O.
Milling Yellow, O O, O G.
Naphthalene Yellow.
Naphthol Yellow S.
Narceïne.
New Yellow G D.
Palatine Orange.

Persian Yellow powder.
Phenoflavine.
Picric Acid.
Quinoline Yellow.
Resorcine Yellow.
Sun Yellow 3 G.
Tartrazine.
Tropaeoline.
Uranine.
Xanthaurine.
Yellow N, F Y, E.

Acid Greens.

Acid Green extra conc., 3 B
  conc., J E E E, Y Y O.
Alkali Green.
Blue Green S.
Eriochlorine, A, B, B B,
  G P S.
Erioglaucine A B, B B, G B,
  R B.
Fast Green (blue), powder.
  ,, Light Green.
Guinea Green B, B N.
Light Green S F (yellow
  shade).
Light Green S F (blue shade).
Milling Green S.
Naphthalene Green V conc.
Neptune Green S.
New Acid Green, 2 B, 3
  B crystals.
Oxamine Green.
Patent Green O, V.
Wool Green S.

Acid Blues.

Alkali Blue B extra, B, 2 B,
  3 B, 4 B, 5 B, 6 B extra, R,
  2 R, 4 R, D, 6 R.
Aniline Blue.
Azine Blue.
Azo Acid Blue B, 4 B, 6 B.
Basle Blue.
Bavarian Blue D B.
Biebrich Acid Blue.
Blue 2 R S, for silk.
Brilliant Blue.
Coomassie Navy Blue.
Cotton Blue B.
Cyanine B.
Cyanol extra, F F.
Eriocyanine A, B.
Fast Acid Blue B, R.
Fast Blue (greenish), B for
  wool, R A for wool, B, R,
  6 B for wool.
Fast Navy Blue 2 M, B M,
  R M.
  ,, Marine Blue B.
  ,, Wool Blue.

Gallanil Indigo P S.
Gallazin A, for dyeing, powder
  for printing.
Gentiana Blue 6 B.
Hoechst New Blue.
Indigo Blue N, S G N.
Induline N N, R extra, B.
Intensive Blue.
Ketone Blue 4 B N solution.
Lanacyl Blue, R, 2 B.
  ,, Navy Blue B.
Lazuline Blue R.
Methyl Blue for cotton.
  ,, ,, for silk.
Milling Blue.
Naphthalene Blue B.
Naphthazine Blue O.
Naphthol Blue R, G.
Naphthyl Blue.
Navy Blue.
New Patent Blue B, 4 B.
New Victoria Black Blue.
Nigrosine 3 G, W, N, O, M.
Patent Blue superior, A, A J I.
Patent Blue V.
Pure Blue extra (greenish)
  powder.
  ,, Soluble Blue.
Red Blue P powder.
Silk Blue I, IV, B E S extra.
Solid Blues R, 3 R, 2 B.
Soluble Blues C 5, 2 X.
Spirit Blue, green shade, red
  shade, 3 R.
Sulphon Acid Blue B.
Thiocarmine R paste.
Urania Blue.
Victoria Black Blue.
Water Blue A D R, 3 B A, 6
  B extra, T B, I N.
Wool Blue B X, S, B B, R.

Acid Violets.

Acid Violet 4 B N, 5 B, 6 B,
  3 B N, 6 B N, 7 B, 3 B pow-
  der, 12 B powder, 3 B extra,
  1 R extra, 2 R, 3 R, 4 B G
  extra, 4 B extra, 8 B extra,
  5 B.
Alkali Violet L R.
Azo Acid Violet 4 R, R extra.
Fast Acid Violet B, 10 B, R,
  A, 2 R.
Formyl Violet S 4 B.
Guinea Violet 4 B.
Lanacyl Violet B R.
Naphthyl Violet.
Neutral Violet O.
Red Violet 4 R S, 5 R S.
Regina Violet.
Victoria Violet 4 B S, 8 B S,
  5 B.
Wool Violet S.

Acid Browns.

Acid Brown G, R, G extra.
Azo Acid Brown.
Chromogen I.
Clayton Wool Brown.
Fast Brown N, 2 B, G, O.
Naphthylamine Brown.
Imperial Orchil Brown B.
Resorcine Brown.

Acid Greys.

Aniline Grey B.
Wool Grey.

Acid Blacks.

Acid Black B, 2 B, S.

Anthracite Black B, R.
Azo Acid Black B, G, R, T L
   conc., 3 B L.
Azo Black.
Biebrich (Patent) Black B O,
   3 B O, 6 B O, R O.
Biebrich (Patent) Black 4 B N,
   4 A N.
Blue Black.
Brilliant Black E, B, 3 B.
Chrome Fast Black B.
Coomassie Black B, G.
Jet Black G, R.
Naphthaline Black 4 B.
Naphthol Black P, B, 3 B, 6 B,
   4 R.

Naphthol Blue Black.
Naphthyl Blue Black N.
Naphthylamine Black 4 B, 6 B,
   D, S.
Nerol B, 2 B.
New Victoria Black B, 5 G.
Palatine Chrome Black A.
Phenol Black S S.
  ,, Blue Black, 3 B.
Phenylene Black.
Sudan Black.
Victoria Black B, G, 5 G.
Wool Black B, 3 B, 4 B, 6 B,
   N 4 B.
Wool Deep Black 2 B, 3 B.

ACID FUCHSINE *v.* Acid Magenta.

ACID GREEN (By.) (D. H.). *Light green S F bluish* (B.), *Vert. sulfo B* (P.), *Acid green M* (M.), *Acid green bluish* (N. J.). 1879. A triphenylmethane derivative. *Sodium salt of dimethyldibenzyldiamidotriphenyl carbinol trisulphonic acid.* Brownish-black powder. Aqueous and alcoholic solution greenish-blue. Concentrated H_2SO_4, yellow solution which becomes green on dilution.

Application.—An acid colour. Dyes *wool* and *silk* in acid bath bluish-green.

ACID GREEN (By.) (F.) (O.). *Light green S F yellowish* (B.), *Vert. sulfo J* (P.), *Acid green extra conc.* (C.), *Acid green D* (M.). 1879. A triphenylmethane derivative. *Sodium salt of diethyldibenzyldiamidotriphenyl carbinol trisulphonic acid.* Green powder. Aqueous and alcoholic solution green. Concentrated H_2SO_4, yellow solution which becomes green on dilution.

Application.—An acid colour. Dyes *wool* and *silk* yellowish-green in acid bath.

ACID GREEN *v.* above and also Fast Green, Guinea Green, Helvetia Green.

ACID MAGENTA. *Acid magenta S, Acid fuchsine, Acid roseine, Acid rubine, Fuchsine S, Rubine S, Cardinal S,* &c. 1877. A triphenylmethane derivative. Mixture of the *sodium or ammonium salts of rosaniline and pararosaniline trisulphonic acid.* Obtained by the action of fuming sulphuric acid on magenta. Green metallic grains or powder. Dissolves easily in water and with difficulty in alcohol, giving a crimson solution. Gives a colourless solution in dilute alkali. Concentrated H_2SO_4 produces a yellow solution which becomes red on dilution.

Application.—An acid colour. Dyes *wool* and *silk* red in acid bath. Not used for cotton. Has only about half the colouring power of magenta.

Impure qualities of acid magenta, containing phosphine, &c., are sold under such names as Acid Maroon, Acid Grenat, Acid Cerise, or Maroon S, Grenadine S, Cerise S, *q.v.*

ACID MAROON. A crude acid magenta.

ACID MAUVE B (H.). *A sulphonated mauvaniline.* Brown granules soluble in water with violet-red solution. Concentrated H_2SO_4, dark red solution which becomes brownish-yellow on dilution.

Application.—An acid colour. Dyes *wool* and *silk* mauve in acid bath.

ACID AND MILLING SCARLET (Br. S. Sp.). 1889. A disazo compound.

$$\left.\begin{array}{l}\text{Alpha naphthol sulphonic}\\ \qquad \text{acid } NW\\ \text{Beta naphthol disulphonic}\\ \qquad \text{acid } R\end{array}\right\rangle \begin{array}{l}\text{Diamido}\\ \text{azoxytoluol.}\end{array}$$
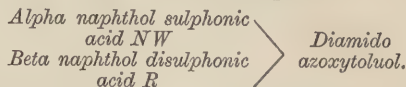
Dark red powder; slightly soluble with scarlet colour in water. Insoluble in alcohol. Alkaline solution orange-red. Concentrated H_2SO_4, solution blue-red which becomes scarlet on dilution.

Application.—An acid colour. Dyes *wool* bright scarlet from an acid bath. Dyed colour is fast to milling and scouring.

ACID MORDANT DYES. This group of dyes is rapidly increasing in importance, since colouring matters belonging to it possess many of the valuable properties of both acid and mordant dyes, combining in many cases the simplicity of application of the former with the fastness of the latter.

They are usually dyed as ordinary acid colours—viz., with addition of sulphuric acid and sodium sulphate, and then, when the bath is exhausted, the material is momentarily removed (this is not always necessary) and bichromate of potash or fluorchrome—usually the latter—is added to the dye bath, the dyeing being continued for half to one hour longer.

ACID MORDANT DYES (for Names of Makers, &c., see Alphabetical Description of Dyes).

Reds.

Alizarin powder S, &c.
Anthracene Red.
Cloth Red O, O B, O G, B,
  3 B, B A, G, 3 G, G A, 3 G A.
Emin Red.
Fast Bordeaux O.
Salicine Red.

Oranges and Yellows.

Alizarin Azo Yellow.
  ,,   Yellow G G, R, R W.
Anthracene Yellow B N, C,
  G G.
Aurotine.
Chrome Orange.
  ,,   Yellow D.
Cloth Orange.
Crumpsall Yellow.
Diamond Flavine G.
  ,,   Yellow G R.
Milling Orange.
  ,,   Yellow.
Mordant Yellow O, R.

Orange R.
Prague Alizarin Yellow G, R.
Terra-cotta R.

Greens.

Acid Alizarin Green G.
Alizarin Dark Green W.
Chrome Patent Green A.
Diamond Green.
Gallanil Green.

Blues.

Acid Alizarin Blue 2 B, G R.
Alizarin Sapphirole.
Gallanil Indigo P.

Blacks.

Acid Alizarin Black.
Anthracene Acid Black, L W,
  S T.
Anthracene Chrome Black 5B
  F.
Anthracite Black B.
Azo Fuchsine B G, S, and G N
  extra (and chrome).

Chrome Patent Black T G,
  T B, T R, T.
Chromotrope 2 B, 4 B, 6 B,
  8 B, 10 B, F B, S B, S, S R
  (and chrome).
Diamond Black, F, N G, N R.
Palatine Chrome Black A.
Phenylene Black.

Violets.

Fast Acid Violet, blue shade.
  ,,   ,,   red   ,,
Gallanil violet.

Browns.

Acid Alizarin Brown.
Anthracene Acid Brown N G.
Chrome Brown O, B O, R O,
  R.
Chromogen I.
Cloth Brown, red shade.
  ,,   yellow shade.
Diamond Brown.
Naphtine Brown.
Resorcine Brown.

ACID ORANGE (G.) *v.* ORANGE II.
ACID PONCEAU (D. & H.). *Fast acid scarlet* (D. & H.). An azo compound.

Beta naphthylamine — Beta naphthol. sulphonic acid.

Is isomeric with *Fast red A, Fast brown 3 B* (Ber.), *Double brilliant scarlet G* (Ber.). Scarlet powder, easily soluble in hot, sparingly in cold, water. Concentrated H_2SO_4 gives a magenta red solution, which yields a brown ppt. on dilution.
Application.—An acid colour. Dyes *wool* scarlet-red in acid bath.
ACID ROSAMINE A (M.) *v.* VIOLAMIN 2 R (M).
ACID ROSEÏNE *v.* ACID MAGENTA.
ACID RUBINE *v.* ACID MAGENTA.
ACID VIOLET (D.). A triphenylmethane derivative. *Sodium salt of benzylrosaniline sulphonic acid.*
Application.—An acid colour. Dyes *wool* in acid bath red-violet.
ACID VIOLET 7 B (B.) (S.C.I.). A triphenylmethane derivative. *Sodium salt of diethyldimethyldiphenyltriamidocarbinol disulphonic acid.* 1886. Brownish-violet powder. Aqueous solution bluish-violet. Concentrated H_2SO_4, brown solution, which becomes green and finally blue on dilution.
Application.—An acid colour. Dyes *wool* and *silk* blue-violet in acid bath.
ACID VIOLET 7 B (L.) *v.* ACID VIOLET 4 B N (B.).

ACID VIOLET 6 B (By.) *v.* ACID VIOLET 4 B N (B.).
ACID VIOLET 6 B (Ber.). A triphenylmethane derivative. *Sodium salt of dimethyldibenzyltriamidotriphenylcarbinol disulphonic acid.* 1889. Bluish-violet powder. Aqueous or alcoholic solution, blue - violet. Concentrated H_2SO_4, yellowish - brown solution which changes to bluish-green on dilution.
Application.—An acid colour. Dyes *wool* or *silk* blue-violet in acid bath.
ACID VIOLET 6 B (G.) *v.* FORMYL VIOLET S, 4 B, (C.).
ACID VIOLET 6 B N (B.) (L.) (S.C.I.). A triphenylmethane derivative. *Sodium salt of tetramethyl-p-tolyltriamidoethoxytriphenylcarbinol sulphonic acid.* 1891. Dark violet powder which gives a blue-violet solution in water. Concentrated H_2SO_4, brownish-yellow solution which on dilution becomes green, and finally blue.
Application.—An acid colour. Dyes *wool* and *silk* bluish-violet.
ACID VIOLET 4 B N (B.) (S.C.I.). *Acid Violet 6 B* (By.); *Acid Violet 7 B* (L.); *Acid Violet N* (M.). A triphenylmethane derivative. *Sodium salt of benzylpentamethyltriamidotriphenylcarbinol sulphonic acid.* 1883. Bluish - violet powder. Aqueous solution bluish-violet. Concentrated H_2SO_4, yellow solution, becoming olive, then green, and finally blue on dilution.
Application.—An acid colour. Dyes *wool* and *silk* blue-violet in acid bath.

ACID VIOLET 3 B N (B.) 1896. Violet powder. Easily soluble in water with violet colour. Alcoholic solution violet. Concentrated H_2SO_4, scarlet solution, on dilution becomes crimson, then violet, and finally blue.

Application.—An acid colour, dyeing somewhat less blue shades than 4 B N.

ACID VIOLET 4 B EXTRA (By.) *v.* FORMYL VIOLET S 4 B (C.).

ACID VIOLET N (M.) *v.* ACID VIOLET 4 B N (B.).

ACID VIOLET 4 R (B.). Constitution not published. 1891. Dyes *wool* and *silk* red-violet in acid bath.

ACID VIOLET 4 R S (B. and M.) *v.* RED VIOLET 4 R S (B.).

ACID VIOLET 5 R S (B.) *v.* RED VIOLET 5 R S (B.).

ACID YELLOW (Ber.) (P.) (Fi.). *Fast yellow* (*B.*) *(By.); Fast yellow G* (*D. & H.*) (*K*) *; Fast yellow extra* (*By.*) *; Fast yellow-greenish* (*D.*) *; Fast yellow S* (*C.*) *; New yellow L* (*K.*). 1878. An azo compound. *Sodium salt of amidoazobenzene disulphonic acid* (*with some monosulphonic acid*). Yellow powder, producing a yellow solution in water, changing to orange on addition of hydrochloric acid. Concentrated H_2SO_4 gives a brownish-yellow solution, which becomes orange-yellow on dilution.

Application.—An acid colour. Dyes *wool* and *silk* yellow in an acid bath.

ACID YELLOW R S (D.), 1875, *v.* RESORCIN YELLOW (Ber.).

ACID YELLOW D (Ber.). An azo compound. *Sodium salt of p-sulphobenzene azo diphenylamine.* 1876. Orange-yellow plates or yellow powder. Aqueous solution orange-yellow from which HCl precipitates violet flocks. Concentrated H_2SO_4, violet solution which precipitates violet flocks on dilution.

Application.—An acid colour. Dyes *wool* and *silk* in acid bath orange-yellow.

ACID YELLOW G *v.* ACID YELLOW.

ACID YELLOW S *v.* NAPHTHOL YELLOW S.

ACIDIMETRY AND ALKALIMETRY.— These terms are used to denote the methods employed for determining the amount of acid and alkali respectively in various substances. In volumetric analysis acids are determined by standard solutions of alkalies, and alkaline bodies by standard solutions of acids. The exact point of neutralisation is shown by an indicator—*i.e.*, a substance which undergoes a distinct change in colour in the presence of the slightest excess of either acid or alkali. The principal indicators used in alkalimetry and acidimetry are *methyl orange, phenolphthaleïn, lackmoid, and litmus.* Numerous others have been recommended, but, except perhaps in special cases, they possess few advantages over those enumerated. It must not be supposed that any one of these indicators is applicable in all cases. Although with the stronger mineral acids in conjunction with caustic alkalies all the indicators show the same neutral point—*i.e*, when the acid and alkali have combined in such proportions as to form a normal alkaline salt, there are numerous cases where one indicator shows a neutral reaction with a normal salt, and another indicator a neutral reaction with an acid salt of the same base. Sodium sulphite (Na_2SO_3), for example, is neutral to phenolphthaleïn, and alkaline to methyl orange, whereas sodium bisulphite ($NaHSO_3$) is neutral to methyl orange, and acid to phenolphthaleïn. There are other cases again where certain indicators are unsuitable on account of a want of precision and sharpness in the end reaction. Phenolphthaleïn, for example, is unsuitable for titrations with ammonia, and litmus is indefinite with acetic, citric, and other organic acids, as well as in the presence of carbonic acid. The characteristics of indicators have been carefully studied by several investigators, particularly by R. T. Thomson,[*] and by Cohn.[†]

Methyl Orange.—This solution may be prepared by dissolving 1 grm. of the colouring matter in a litre of water, 2 or 3 drops of which will be sufficient for each titration. An alkaline solution is of a very pale yellow colour, but with the slightest excess of acid a pink coloration is developed. It is unaffected by carbonic acid or sulphuretted hydrogen. Carbonates can, therefore, be titrated in the cold.

Lackmoid is prepared by the action of sodium nitrate on resorcine. 1 grm. of the colouring matter is dissolved in 100 c.c. of a mixture of equal parts alcohol and water. Alkaline solutions are blue, and acid solutions red—the change being sharp and well defined. Its properties as an indicator are similar to methyl orange. Paper prepared with lackmoid has many advantages over the solution. Lackmoid paper admits of the determination of carbonates and bicarbonates with more precision than the solution. The paper is also of great service in the case of highly-coloured solutions, and in titrating chromates and chromic acid, *bichromates* being exactly neutral to lackmoid.

Phenolphthaleïn is a most useful indicator. 1 grm. of the substance is dissolved in 100 c.c. of 90 per cent. alcohol. The liquid is colourless in neutral and acid solutions, but the faintest excess of alkali gives an intense red colour. Two or three drops are sufficient for each titration. It is especially serviceable in the estimation of acids with standard solutions of caustic potash or soda. It is not available for ammonia, nor for the estimation of carbonates, unless the liquid is

[*] *Chem. News*, vol. xlvii., pp. 123, 135, 184; vol. xlix., pp. 32, 38, 119; vol. lii., pp. 18, 29.
[†] "Indicators and Test Papers," Cohn, 1899.

well boiled so as to completely expel all carbonic acid. For many weak organic acids it is the only indicator which gives good results. It is also exceedingly useful in the estimation of free caustic alkali in such substances as soap, as well as for free fatty acids in oils, and determination of the saponification equivalent of oils, &c., &c.

Litmus.—About 10 grms. of solid litmus are ground and treated with 80 per cent. alcohol to remove certain colouring matters not affected by acids and alkalies. The residue is repeatedly treated with cold water, and the solution obtained acidulated with sulphuric acid and boiled. Barium hydrate is now cautiously added to precipitate the sulphuric acid, and the baryta in its turn precipitated by carbonic acid. The liquid is filtered and made up to half a litre. It should be kept in a bottle to which air has free access. Litmus is not serviceable in the presence of free carbonic acid, and it gives no definite end reaction with most of the organic acids. With mineral acids and caustic alkalies, litmus, like other indicators, is sharp and delicate, but it possesses no advantages over methyl orange. With the two indicators, methyl orange and phenolphthaleïn, practically all acidimetric and alkalimetric operations can be performed.

Preparation of Standard Solutions, Normal Solutions. — Although some difference of opinion has existed among chemists regarding the significance of normal solutions used in volumetric analysis, most chemists are agreed that normal solutions are such that they contain in 1 litre the hydrogen equivalent of the active reagent in grammes. In other words, a litre of a normal solution of any substance is of such a strength that it will exactly neutralise, replace, or oxidise 1 grm. of hydrogen or its equivalent. Normal solutions are, therefore, based upon equivalent weights —*not molecular weights.* The following table shows a few examples of normal solutions :—

Potassium hydrate,	.	56 grms.	KOH	per litre.
Ammonium hydrate,	.	17 ,,	NH_3	,,
Sodium carbonate,	.	53 ,,	Na_2CO_3	,,
Hydrochloric acid,	.	36·5 ,,	HCl	,,
Sulphuric acid,	.	49 ,,	H_2SO_4	,,
Nitric acid,	.	63 ,,	HNO_3	,,
Sodium chloride,	.	58·5 ,,	NaCl	,,
Silver nitrate,	.	170 ,,	$AgNO_3$	,,
Oxalic acid,	. .	63 ,,	$C_2H_2O_4,2H_2O$	,,
Potassium permanganate,	31·6 ,,	KMnO_4	,,	

A given volume of any of the above *alkaline* solutions will exactly neutralise the same volume of any of the *acid* solutions, and *vice versâ.* A given volume of the sodium chloride solution will exactly precipitate the silver in the same volume of silver nitrate solution. And again the potassium permanganate solution will completely oxidise exactly the same volume of oxalic acid. It will be observed that in the case of dibasic acids

one-half of the molecular weight in grammes forms the normal solutions ; also that one-fifth of the molecular weight of potassium permanganate is taken, since one part of this salt is capable of oxidising five parts of hydrogen. The advantages of having solutions made up on this principle are manifold. If, for example, it is required to know the amount of carbonate of soda in a sample of refined soda ash, the number of cubic centimetres of any normal acid required to neutralise 5·3 grms. of the sample expresses the percentage. If 3·1 grms. of the sample were taken, the number of cubic centimetres (c.c.) of any acid required would correspond to the percentage of sodium oxide present. In like manner, by titrating 4·7 grms. of a sample of caustic potash or potassium carbonate with a normal acid, the number of c.c. required to effect neutralisation gives the percentage of potassium oxide (K_2O) present. By varying the amount of substance weighed out in the proportion of equivalent weights, the use of normal solutions enables the percentage of the body sought to be directly expressed. In many cases it is found in practice more convenient to employ weaker solutions than those above mentioned. For such purposes seminormal, quintinormal, decinormal, and centinormal solutions (indicating solutions one-half, one-fifth, one-tenth, and one-hundredth as strong as normal solutions) are frequently used, and are usually abbreviated $\frac{N}{2}$, $\frac{N}{5}$, $\frac{N}{10}$, and $\frac{N}{100}$ respectively. In certain technical analyses where a standard solution is used for the determination of one substance only, it may be found simpler and more advantageous to employ an empirical standard solution of such a strength that every cubic centimetre shall represent either one decigramme, centigramme, or milligramme of the body to be estimated. For example, supposing a number of analyses of refined alkali (sodium carbonate) are constantly being made for sodium oxide only. A standard acid might be prepared, so that each cubic centimetre neutralised 0·01 grm. Na_2O, when the number of cubic centimetres required to neutralise 1 grm. of the sample would directly express the percentage.

Normal Sulphuric Acid.—1 c.c. = ·049 grm. H_2SO_4. About 30 c.c. of pure concentrated sulphuric acid are diluted with four or five times as much water, the mixture allowed to cool, and then made up with more water to a litre. This solution will now require standardising—that is, its strength must be accurately ascertained. For this purpose 1·06 grms. of pure anhydrous sodium carbonate are dissolved in about 100 c.c. of water and a few drops of methyl orange added. The sulphuric acid solution is now run in from a burette until a faint pink colour is produced. The

operation is best performed in a white porcelain dish, stirring the liquid with a glass rod whilst the acid is being run in. If the acid were strictly normal, exactly 20 c.c. would be required, but in all probability it will be found too strong. Suppose 19·5 c.c. of the acid solution were required, it is evident that this amount contains as much sulphuric acid as 20 c.c. of strictly normal acid. Consequently, in order to make the acid of the required strength, all that is necessary is to accurately measure the volume of solution and add water in the proportion of ·5 c.c. to every 19·5 c.c. Another titration with 1·06 grms. of pure sodium carbonate is now made, when, if care has been duly taken, exactly 20 c.c. of the acid will be required. One standard acid at least should be prepared with the greatest care, leaving no doubt of its accuracy. As sulphuric acid can be very accurately estimated gravimetrically by means of barium chloride, the volumetric determination may oe controlled in this way. It is important to bear in mind that the sulphuric acid used should be free from sulphates, otherwise the precipitation method would give too high results. The acid, on ignition, should leave no appreciable residue, neither should it contain ammonium sulphate. In order to control the strength of normal sulphuric acid gravimetrically, 10 c.c. may be withdrawn by means of an accurate pipette, and diluted with about 150 c.c. of water. A few drops of hydrochloric acid are added, and the liquid heated to the boiling point, when a hot solution of barium chloride is slowly and carefully added until no further precipitate takes place. The solution is now kept hot for two or three hours on the water bath (the beaker being covered with a clock glass to prevent evaporation), after which time the clear liquid is poured on a filter, and the precipitate treated with boiling water. The barium sulphate is thus washed two or three times by decantation, when it is wholly transferred to the filter and washed with hot water until free from either barium or chlorine, shown respectively by adding sulphuric acid or silver nitrate to a little of the filtrate. The filter and contents are dried, the precipitate transferred to a weighed crucible, the paper incinerated separately and added to the bulk, and the whole heated, at first gently and then to bright redness, for 10 minutes, cooled, and weighed. 10 c.c. of normal sulphuric acid treated in this manner should give 1·165 grms. of $BaSO_4$, corresponding to 0·490 grm. of sulphuric acid. From the normal sulphuric acid $\frac{N}{2}$ $\frac{N}{5}$, and $\frac{N}{10}$ solutions may be prepared by carefully diluting with the requisite amount of distilled water.

Normal Hydrochloric Acid.—1 c.c. = ·0365

grm. of HCl. Hydrochloric acid boiling under the ordinary atmospheric pressure has a constant composition. It contains 20·2 per cent. HCl, and has a specific gravity of 1·10. If 181 grms., or 164·5 c.c., of this acid be diluted to a litre it forms an approximately normal solution, which may be standardised volumetrically exactly in the same manner as sulphuric acid, 1·06 grms. of pure sodium carbonate requiring 20 c.c. of the normal acid as with sulphuric.

Normal Caustic Soda.—1 c.c. = ·040 grm. of NaHO. About 50 grms. of pure caustic soda of commerce (purified by alcohol) are dissolved in a litre of water and the solution (25 c.c. or 50 c.c.) titrated with normal sulphuric acid and methyl orange. The solution will most probably be found too strong. It is carefully diluted with the requisite amount of water (as in the adjustment of sulphuric acid described above), and again titrated when 25 c.c. should be exactly neutralised by 25 c.c. of the normal acid.

ACME YELLOW (L.) *v.* Resorcine Yellow (Ber.)

ACORN GALLS *v.* Knoppern.

ACRIDINE ORANGE (L.). An acridine derivative. *Zinc chloride double salt of tetramethyldiamido acridine hydrochloride.* Allied to phosphine.

$$(\text{Acridine} = C_6H_4\!<\!\genfrac{}{}{0pt}{}{CH}{N}\!>\!C_6H_4)$$
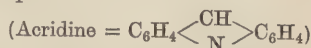
1889. Orange powder. Aqueous solution, orange with greenish fluorescence, becoming red on addition of hydrochloric acid. Concentrated H_2SO_4, very pale coloured solution with greenish fluorescence, becoming red, and finally orange on dilution.

Application.—A basic colour. Not suitable for *wool*. Dyes *silk* in neutral bath orange with green fluorescence. Dyes *cotton* bright orange on tannic acid and tartar emetic prepare.

ACRIDINE ORANGE R EXTRA (L.). An acridine derivative. *Hydrochloride of tetramethyldiamidophenyl acridine.* 1889. Orange red powder giving an orange solution in water. Concentrated H_2SO_4, yellow solution with green fluorescence, red on dilution.

Application as Acridine Orange.

ACRIDINE RED B, 2 B, 3 B (L.). A diphenylmethane derivative. *Chloride of tetraethyldiamidooxydiphenyl carbinol.* 1891. Allied to rhodamine and pyronine. Brown powder which dissolves in water or alcohol, giving a red solution with yellow fluorescence. Addition of hydrochloric acid to aqueous solution changes colour to orange. Concentrated H_2SO_4, yellow solution, which becomes red on dilution.

Application.—A basic dye. Unsuitable for *wool*. Dyes *silk*, or *cotton* mordanted with tannic acid and tartar emetic, rose red, yellower than pyronine.

ACRIDINE SCARLET (L.). Mixture of pyronine or acridine red and acridine yellow.

ACRIDINE YELLOW (L.). An acridine derivative. *Hydrochloride of diamidodimethyl acridine.* 1889. Yellow powder, giving a yellow solution with green fluorescence in water or alcohol. Concentrated H_2SO_4, light yellow solution, giving a yellow precipitate on dilution.

Application.—A basic dye. Unsuitable for *wool.* Dyes *silk* yellow with green fluorescence. Dyes *cotton* yellow on tannin and tartar emetic mordant.

ADIPO-CELLULOSES *v.* COTTON.

ALBUMEN. *Blood albumen* (*Serum albumen*) is a nitrogenous substance obtained by evaporating, at a low temperature, the blood of animals. It comes into commerce in the form of dark brown scales. It is soluble in cold water, but insoluble in alcohol and in ether. Unlike egg albumen, it is not coagulated by agitation with ether.

Egg Albumen is prepared by evaporating white of egg to dryness at moderate temperatures; the residue comes into the market as light yellow horny flakes. It resembles blood albumen to a great extent, but is a very much purer article and, of course, more costly. Both kinds of albumen are used in the dyeing and printing of calico, and, to some extent, in woollen printing.

Properties. — Solutions of albumen are coagulated on heating to about 70° C., a white insoluble substance being produced; and precipitates are caused by the addition of mineral acids or solutions of various metallic salts. Metaphosphoric acid, or a solution of a metaphosphate (*e.g.*, $NaPO_3$) and acetic acid coagulate albumen. Ortho- and pyrophosphoric acids, acetic and carbonic acids give no precipitates. Sodium chloride only causes a precipitate on the addition of acetic acid to the albumen solution. Dilute potash and soda do not produce precipitates.

Albumen is similar in composition to wool and silk, and when coagulated and treated with colouring matters, behaves in a similar manner to those fibres.

The dry substance may be kept indefinitely, but if it be damp or in the liquid state putrefaction soon sets in, this process being accentuated in warm weather. An addition of a small amount of borax or sodium bisulphite retards decomposition of the solution. Turpentine is used for the same purpose.

Uses.—Albumen is employed for fixing insoluble pigments, such as ultramarine, aniline-colour lakes, &c., by mixing the finely-powdered colouring matter with the cold albumen solution. After printing the mixture on the calico the latter is steamed. The heat causes the albumen to become coagulated, and encloses minute particles of the colouring matter within the fibre, thus permanently fixing it.

For use with the coal-tar colours the cotton is printed with the albumen and steamed, or passed through dilute mineral acid, which has the same effect, and eventually dyed, the colour appearing only on the parts printed with albumen. Weight for weight, blood albumen has greater thickening power than egg albumen, but the latter is preferable for light colours.

Albumen has been used as a discharge on manganese bistres.[*]

Examination of Albumen.—A solution of albumen is sold at a strength of about $3\frac{1}{2}$° Tw. It is often adulterated with 2 or 3 per cent. of zinc salts to thicken it. For the detection of *zinc*, the solution is evaporated, ignited gently, and the zinc dissolved out with dilute acid. On the addition of ammonia and ammonium sulphide a white precipitate of zinc sulphide is produced.

Test for Gelatin.—Add to the aqueous solution a little acetic acid, filter, boil the filtrate, neutralise, cool, and filter. Add to part of the filtrate a solution of tannic acid, if a white precipitate is formed, which is mostly soluble in alcohol, gelatin was present. If insoluble in alcohol, it is probably albumen which has passed through.

V. Ganthier [†] makes use of the following test as a means of distinguishing between egg albumen and blood albumen. The reagent consists of 250 c.c. caustic soda solution, 50 c.c. of a solution of copper sulphate, 100 c.c. of glacial acetic acid. On mixing a solution of 2 grms. of the substance with 10 c.c. of this reagent, egg albumen may be readily recognised by rendering the liquid turbid, and forming a flaky precipitate, while in the case of blood albumen no change takes place.

P. Carles [‡] tests commercial egg albumen as follows:—2 grms. of the sample are dissolved in a small quantity of water (a possible adulteration with flour will be detected here) and gradually diluted with constant stirring to 200 c.c. If free from coagulated albumen this solution will be clear. 100 c.c. of this are taken, and 35 c.c. of a 1 per cent. pure tannin solution added, and a little potassium bitartrate. The mixture is well shaken, then thrown on a plain filter, and the clear filtrate divided into two equal parts in two exactly similar tubes. To one a few drops of transparent gelatin is added; to the other a like quantity of tannin solution. If both remain clear the egg albumen is pure and of good quality. If the gelatin solution cause a precipitate, it shows that the egg albumen is weak and of poor quality, either from a portion having coagulated by overheating in the course of

* *Journ. Soc. Chem. Ind.*, 1896, p. 449.
+ *Journ. Soc. Dyers and Col.*, 1886, p. 47.
‡ *Journ. Soc. Chem. Ind.*, 1897, p. 767.

manufacture or by the fraudulent addition of non-coagulating matter. On the other hand, if the tannin solution gives a precipitate, it is due to the presence of gelatin, which has about four times greater precipitating power for tannin than egg albumen ; but, since it is not coagulated by heat, it is valueless for many technical purposes, such as clarifying liquids, fixing dyes, &c.

If another 100 c.c. of the solution be gradually heated on the water bath, the egg albumen will be coagulated, and the filtrate from a genuine substance will give no precipitate with tannin. Any gelatin present would cause a precipitate, which should be filtered off, and the filtrate tested for dextrin, gums, &c.

ALCOHOL. — C_2H_5OH (*Ethyl alcohol ; spirits of wine*). The alcohols form an important and numerous class of organic compounds, but the term "alcohol" when applied without qualification is understood to refer to ethyl alcohol, the product of the vinous fermentation of sugar. It is the pure essence or spirit which imparts to wine and other fermented liquids their intoxicating property. The juice of grapes already contains sugar as well as a ferment, and when exposed under suitable conditions fermentation ensues, resulting in the splitting up of the sugar (grape sugar or glucose) into alcohol and carbon dioxide :—

$$\underset{\text{Glucose.}}{C_6H_{12}O_6} \quad = \quad \underset{\text{Alcohol.}}{2C_2H_6O_2} \quad + \quad \underset{\text{Carbon dioxide.}}{2CO_2}$$

Although the above simple equation represents the chief reaction which takes place during vinous fermentation, it is not by any means the only change which occurs. Other alcohols, glycerin, and succinic acid are always produced, as well as traces of many other bodies. When alcohol is obtained from grain (barley, maize, rice, &c.), the starch of the seed must first be converted into sugar. Alcohol may be prepared synthetically from acetylene, C_2H_2. In the presence of nascent hydrogen, acetylene forms ethylene, C_2H_4, which combines with sulphuric acid to produce sulphovinic acid, $C_2H_5HSO_4$, and this, on distilling with water, produces alcohol.

Rectified Spirit of Wine is the name given to the strongest alcohol which is produced by ordinary distillation. The rectified spirit of the British Pharmacopœia contains 84 per cent. of absolute alcohol, and has a density of ·838.

"**Proof Spirit**" is a name adopted by the Excise to indicate a spirit of a certain strength. By Act of Parliament proof spirit is defined to be a liquid of such density that at 51° F. 13 volumes shall weigh the same as 12 volumes of distilled water at the same temperature. Such a liquid has a density of ·91984 at 15·5° C., and contains 49·24 per cent. by weight of alcohol and 50·76 of water. Formerly the Excise tested the strength of

spirits by pouring a certain amount on gunpowder and applying a light. If the alcohol was above a certain strength—*i.e.*, "proof"—the gunpowder ignited, but if weaker the excess of water prevented the ignition of the gunpowder, and the spirit was therefore said to be "under proof."

Methylated Spirits, or methylated alcohol, consists principally of ethyl alcohol, but is mixed with other substances with a view of rendering it unfit for drinking purposes, and is exempted from excise duty. There are various qualities ; the best spirit, which can only be obtained by special permission of the Excise authorities, contains 90 per cent. of rectified spirit of wine and 10 per cent. of wood spirit (commercial methyl alcohol). The common methylated spirit contains, in addition to the above, a small quantity of mineral naphtha. Another variety known as *methylated finish* contains in place of mineral naphtha a gum resin in the proportion of not less than 3 ounces to the gallon, and is used by varnish makers, &c.

Properties.—Pure alcohol, free from water, known as absolute alcohol, is a colourless mobile liquid, possessing an agreeable spirituous smell and a burning taste. It volatilises somewhat rapidly at the ordinary temperature, and boils at 78·4° C. It solidifies at −130·5° C. Its specific gravity at 15·5° C. is ·7938. Alcohol possesses a great affinity for water. It mixes with it in all proportions with evolution of heat and contraction in volume. Absolute alcohol exposed to ordinary air absorbs water from it, becoming weaker. A mixture of water and alcohol cannot be completely separated by fractional distillation ; in order to withdraw all the water it is necessary to distil in presence of a substance (such as potassium carbonate) having a still greater attraction for water. Alcohol is very inflammable, burning with a slightly luminous flame. Alcohol dissolves a great number of organic compounds, such as resins, fatty acids, volatile oils, phenol, creosote, glycerin, soaps, many hydrocarbons and organic bases. The caustic alkalies, and generally speaking the metallic chlorides, bromides, iodides, and acetates, are soluble in alcohol, while the carbonates, borates, sulphates, phosphates, oxalates, and tartrates are usually insoluble. Most gases dissolve more freely in alcohol than in water. Oxidising agents (such as chromic acid and permanganic acid) convert alcohol into aldehyde and acetic acid. Formic, acetic, oxalic, hydrochloric, and other acids decompose alcohol with the formation of the ethereal salts.

Uses.—In addition to its use as a beverage, ethyl alcohol is largely employed as a solvent for medicinal drugs and essential oils, and in the preparation of perfumes and essences. Pure alcohol, particularly on account of its

solvent properties, is of great value in the chemical laboratory. In dyeing and calico-printing, methylated spirit (which should be of the best quality) is used for dissolving certain colouring matters. For these purposes it is important that the methylated spirit be free from aldehyde and acetone. Alcoholic solutions of some coal-tar colours with certain resins (shellac, &c.) are used in the preparation of highly-coloured varnishes. Methylated spirit is also used in the manufacture of transparent soap and for burning in lamps.

Examination and Analysis.— *Water* may be detected in alcohol by the addition of

SPECIFIC GRAVITY OF ETHYL ALCOHOL AND PERCENTAGE BY WEIGHT AT 15·5° C. (60° F.)—(*Fownes*).

Specific Gravity.	Per cent. by weight C_2H_6O.	Specific Gravity.	Per cent. by weight C_2H_6O.
0·9991	0·5	0·9160	51
0·9981	1	0·9135	52
0·9965	2	0·9113	53
0 9947	3	0 9090	54
0 9930	4	0·9069	55
0·9914	5	0·9047	56
0·9898	6	0 9025	57
0·9884	7	0·9001	58
0·9869	8	0·8979	59
0·9855	9	0·8956	60
0·9841	10	0·8932	61
0·9828	11	0·8908	62
0·9815	12	0·8886	63
0·9802	13	0·8863	64
0·9789	14	0·8840	65
0·9778	15	0·8816	66
0 9766	16	0·8793	67
0·9753	17	0·8769	68
0·9741	18	0·8745	69
0·9728	19	0·8721	70
0·9716	20	0·8696	71
0·9704	21	0·8672	72
0 9691	22	0·8649	73
0·9678	23	0 8625	74
0·9665	24	0·8603	75
0·9652	25	0·8581	76
0·9638	26	0·8557	77
0·9623	27	0 8533	78
0·9609	28	0·8508	79
0·9593	29	0·8483	80
0·9578	30	0·8459	81
0·9560	31	0·8434	82
0·9544	32	0·8408	83
0·9528	33	0·8382	84
0·9511	34	0·8357	85
0·9490	35	0·8331	86
0·9470	36	0·8305	87
0 9452	37	0·8279	88
0·9434	38	0·8254	89
0·9416	39	0·8228	90
0·9396	40	0·8199	91
0·9376	41	0·8172	92
0·9356	42	0·8145	93
0·9335	43	0·8118	94
0·9314	44	0·8089	95
0·9292	45	0·8061	96
0·9270	46	0·8031	97
0·9249	47	0·8001	98
0·9228	48	0·7969	99
0·9206	49	0·7938	100
0·9184	50		

gently-ignited copper sulphate. The greyish-white powder will acquire a blue colour if a notable quantity of water be present. A more delicate test consists in introducing a crystal of potassium permanganate. If so little as $\frac{1}{2}$ per cent. of water be present the liquid assumes a pink colour. *Oily* and *resinous* matters may be detected by diluting the spirit with water, when they impart a milky appearance to the liquid. *Aldehyde*, when present in quantity, imparts a brown colour to the liquid when heated with caustic soda. *Solid matter* may be detected and estimated, if present, by evaporating 100 c.c. to dryness and weighing the residue. Afterwards, any *mineral matter* may be estimated by igniting the residue and weighing again. Methylated spirit to be used for dissolving any particular colour should be compared with a sample known to be of good quality for the purpose. If, for example, the colour be magenta, pour 50 c.c. or 100 c.c. of the pure methylated spirits into a beaker or glass cylinder, and a similar amount of the sample to be tested into another vessel. Then add the same amount of magenta (say 5 c.c. of a concentrated solution in pure alcohol) to each, and note the colour. If aldehyde or acetone were present the magenta would turn bluer—approaching a violet—according to the amount of impurity present.

The amount of water present in commercial alcohol, or, in other words, the strength of the spirit, may be readily ascertained by taking the density, either with a delicate hydrometer or a specific gravity bottle, and referring to tables.

Determination of Alcohol by Distillation. —In the presence of fixed solid matter (such as with wine or beer) a given volume of the liquid, 50 c.c. or 100 c.c., at 15·5° C , is carefully weighed. The liquid is made slightly alkaline with caustic soda, diluted with twice its volume of water, and transferred to a small flask or retort connected with a Liebig's condenser. It is advisable to add a small amount (about $\frac{1}{10}$ grm.) of tannin to prevent frothing. The flask is gently heated, and the distillate collected in a flask holding 100 c.c. When nearly full the operation is arrested, and the distillate well mixed and brought to a temperature of 15·5° C., and made up exactly to 100 c.c. with distilled water of the same temperature, and weighed. The density is then taken, and the percentage of alcohol present in the distillate found by reference to the tables. The percentage of alcohol thus found, multiplied by the weight of distillate and divided by the weight of sample taken, gives the percentage of absolute alcohol by weight contained in the sample.

ALDEHYDE. *Acetaldehyde*, CH_3CHO. Aldehyde is formed by the partial oxidation of alcohol. Commercially, it is obtained

from the "first runnings" of alcohol stills in the rectification of alcohol. It may be prepared by distilling a mixture of alcohol, sulphuric acid, and manganese dioxide. Aldehyde is a colourless, mobile, and very volatile liquid, having a pungent, suffocating odour. It is very inflammable. It has a density of ·789 at 15·5° C., and boils at 20·8°. It is miscible in all proportions with water, alcohol, and ether. On the addition of calcium chloride to its aqueous solution aldehyde separates as an ethereal layer. Aldehyde is readily oxidised to acetic acid, and thus forms a powerful reducing agent. When treated with caustic soda it forms a brown resinous mass, upon which property its detection in alcohol is based.

Aldehyde was formerly used in the preparation of aldehyde green, a colouring matter which is practically obsolete.

ALDEHYDE GREEN. *Aniline green, Usèbe's green.* A triphenylmethane derivative. *A quinoline derivative of rosaniline* obtained by the action of aldehyde upon aniline and treatment of the product with sodium thiosulphate. 1862. Now very seldom used. Amorphous green powder insoluble in water, but easily soluble in a mixture of water, alcohol, and sulphuric acid.

Application.—Dyes *silk* green from the acid solution obtained as above.

ALDER BARK (*Alnus glutinosa*) is used to some extent for producing yellow upon leather, and as a tannin.

ALGINE is a mucilaginous substance resembling gum arabic, obtained from red algæ. The seaweeds are treated with a boiling solution of sodium carbonate, which dissolves the alginic acid in the form of sodium alginate, leaving the cellular tissue of the plant behind. The filtered alkaline solution is treated with hydrochloric acid, which precipitates the alginic acid as an amber-coloured gelatinous mass. The precipitate is filtered by means of a filterpress, re-dissolved in a solution of sodium carbonate, evaporated to a thick consistence, and dried in porcelain vessels. The sheets are then steeped in hydrochloric acid to remove the soda.

Soluble algine, which is an alkaline alginate, appears in the form of flexible transparent laminæ of the following composition :—

Water,	18·22	per cent.
Organic matter,	59·05	,,
Sodium carbonate,	18·05	,,
Neutral salts,	2·87	,,
Insoluble substances,	1·81	,,

Algine is very similar to gelatin, but it differs from the latter by not coagulating to a jelly, and by not being precipitated by tannin. It differs from albumen by not being coagulated by heat. It differs from gum arabic because it is precipitated from its solutions by the mineral acids and by oxalic, tartaric, citric, lactic, and picric acids.

The solutions of algine are very viscid. It has fourteen times the viscosity of starch and thirty times that of gum arabic. This property enables it to be used in tissueprinting as a thickener in place of gum or dextrin.

It gives cloths a thick, soft, elastic feel, and furnishes a transparent dressing, which may be made insoluble and impermeable by passing the cloth through a dilute solution of algine and then through very dilute hydrochloric acid, which fixes the alginic acid on the fibres in an insoluble state.

The alkaline alginates may be used as salts for "dunging," for fixing iron and aluminium mordants upon cotton tissues.

Aluminium alginate dissolved in dilute ammonia serves to render cloth waterproof by simply steeping the material in the solution and driving off the ammonia.

Aluminium alginate is used as a mordant.

ALIZARIN DYES. The name *Alizarin* is applied to the chief madder colouring principle (*v.* MADDER); to several closely related artificial dyes, one of which is identical with natural alizarin ; and also generically to designate a large and important group of dyes of varied hue, mostly derivatives of *anthracene* (*q.v.*).

This group of artificial products now includes dyestuffs yielding an almost complete range of shades, and characterised (usually) by great permanence or fastness towards light, milling, wear, and other influences. As a class, the alizarin dyes are more closely related to the natural dyewoods than are other groups of coal-tar colours, not only in chemical constitution but also in mode of application and character of colour obtained. The alizarin dyes are, however, much more numerous and produce shades much more varied in hue, as well as brighter, cheaper, and faster, than the older dyewoods.

Artificial alizarin was discovered in 1868 by Graebe and Liebermann, who first succeeded in obtaining anthracene from natural alizarin, and subsequently in synthesising alizarin from anthracene. In 1869, Perkin, simultaneously with these chemists, introduced the much improved and cheaper process of manufacture which is, with slight modification, now employed.

Anthracene, the raw material of the manufacture, exists in considerable quantities in coal tar (*v.* ANTHRACENE). It is converted into *anthraquinone* by oxidation with chromic acid, and the latter is then converted into *alizarin* by the following series of reactions:—

1. $C_6H_4\!<^{CH}_{CH}\!>C_6H_4 + 30$

   Anthracene.

   $= C_6H_4\!<^{CO}_{CO}\!>C_6H_4 + H_2O$

   Anthraquinone.

2. $C_6H_4\!<^{CO}_{CO}\!>C_6H_4 + H_2SO_4$

   $= C_6H_4\!<^{CO}_{CO}\!>C_6H_3 . HSO_3 + H_2O$

   Anthraquinone monosulphonic acid.

3. $C_6H_4\!<^{CO}_{CO}\!>C_6H_3 . HSO_3 + 2NaOH$

   $= C_6H_4\!<^{CO}_{CO}\!>C_6H_2 (OH)_2$

   Alizarin.

   $+ Na_2SO_3 + H_2$

   Sodium sulphite.
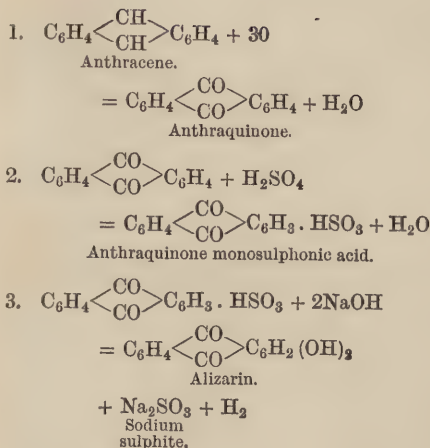
Alizarin is thus a *dihydroxy-anthraquinone*, the two hydroxyl (OH) groups being in *ortho* position as represented by the formula—

$$C_6H_4\!<^{CO}_{CO}\!>C_6H_2\!<^{OH \ (1)}_{OH \ (2)}$$
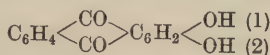
Of the ten isomeric bodies of this constitution alizarin alone is a useful dyestuff, and the presence of two hydroxyl groups in the position indicated above is an essential feature in colouring matters of this type, all true alizarin colours being derivatives of this particular dihydroxyanthraquinone. For instance, the four colouring matters—*anthrapurpurin, flavopurpurin, purpurin,* and *anthracene brown*—are isomeric *trihydroxyanthraquinones;* two of the hydroxyls in each case being in the positions 1 : 2, but the position of the third hydroxyl varying.

The constitution of other alizarin colours is indicated under the separate headings.

ALIZARIN. *Alizarin V I* (B.) ; *Alizarin V* (L.) ; *Alizarin 1e* (By.) ; *Alizarin No. 1* (M.) ; *Alizarin No. 1 B new* (M.) ; *Alizarine P* (Brit. Aliz. Co.) ; *Alizarin red N B* ; *Alizarin blue shade.* An anthracene derivative. *Dihydroxyanthraquinone* ((OH) = 1 : 2). When pure, forms reddish-yellow powder or orange-red needle crystals. Melts at 289° to 290° C., but sublimes without decomposition at a much lower temperature (about 120° C.). It is insoluble in water or cold alcohol ; but soluble in hot alcohol, with a yellowish-red colour. Soluble also in ether, benzene, glacial acetic acid, or glycerine. Soluble in ammonia with a purple colour, in caustic soda with a blue-violet colour, but is precipitated unchanged from these alkaline solutions by acids. Soluble in concentrated H_2SO_4 with a brown colour, but reprecipitated unchanged on dilution. Sulphuric anhydride forms a sulphonic

acid (Alizarin S). By oxidation with manganese peroxide or arsenic acid it is converted into *purpurin* ; fuming nitric acid (cold) forms *nitropurpurin* ; dilute nitric acid (boiling) gives *phthalic and oxalic acids.* Nitrous acid produces *beta-nitro alizarin* (*alizarin orange*).

Towards alkalies and bases generally, alizarin behaves as a weak acid, forming salts in which the metal replaces the hydrogen in the hydroxyl groups. The lakes formed with the heavy metals and the alkaline earths are insoluble in water, but the compounds with the alkalies are easily soluble. All the colour lakes are strongly coloured, and upon their production the dyeing with alizarin depends.

Commercial alizarin is sold in the form of a yellow paste usually containing 20 per cent. of dry substance ; occasionally it is met with as dry powdery lumps containing glycerin, starch, &c. In the commercial products the alizarin contains water of hydration which renders it readily miscible with water. If allowed to become dry and dehydrated, it cannot be mixed with water unless again hydrated by dissolving in alkali and reprecipitating with acid.

Assay of Alizarin Paste.—(a) *Moisture.*— 2 to 5 grms. of the paste are dried to constant weight, at 100° to 105° C., in a small platinum capsule. (b) *Ash.*—The residue from (a) is ignited to redness. The ash should not exceed 1 per cent., and should be quite free from iron. It consists mainly of sodium and calcium salts. (c) *Colouring matter.*—This is usually estimated in a comparative manner by means of dyeing trials on cotton cloth mordanted in stripes with aluminium and iron. The standard cloth for this purpose is known as S.K.G. cloth, and contains five stripes—viz., strong and weak aluminium mordant, strong and weak iron mordant, and a mixture of aluminium and iron.

Applications.—A mordant dye. Applied to all fibres in conjunction with metallic mordants, the most important metallic lakes having the following colours :—

Chromium,	.	Claret or maroon.
Aluminium,	.	Bright red.
Iron,	. .	Purple.
Tin,	. .	Orange.
Uranium,	.	Grey.

ALIZARIN No. I. (M.) *v.* ALIZARIN.
ALIZARIN No. 1 B NEW (M.) *v.* ALIZARIN.
ALIZARIN No. 1 e (By.) *v.* ALIZARIN.
ALIZARIN No. 6 (M.) *v.* PURPURIN.
ALIZARIN C A (B. A. Co.) *v.* FLAVOPURPURIN.
ALIZARIN G D (B.) *v.* ANTHRAPURPURIN.
ALIZARIN G 1 (B.) *v.* FLAVOPURPURIN.
ALIZARIN O G (By.) *v.* ALIZARIN ORANGE

2

ALIZARIN O K (By.) *v.* ALIZARIN ORANGE.
ALIZARIN P (B.A.Co.) *v.* ALIZARIN.
ALIZARIN R G (B.) *v.* FLAVOPURPURIN.
ALIZARIN R X (M.) *v.* ANTHRAPURPURIN.
ALIZARIN 5 R D (L.) *v.* FLAVOPURPURIN.
ALIZARIN 3 R F (L.) *v.* ANTRAPURPURIN.
ALIZARIN S, 2 S and 3 S (B.) *v.* ALIZARIN RED S, 2 S AND 3 S.
ALIZARIN S C (B.A.Co.) *v.* ANTHRAPURPURIN.
**ALIZARIN S D G** (M.) *v.* FLAVOPURPURIN.
ALIZARIN S X (B.) *v.* ANTHRAPURPURIN.
ALIZARIN S X EXTRA (By.) *v.* ANTHRAPURPURIN.
ALIZARIN V. (L.) *v.* ALIZARIN.
ALIZARIN VI. (B.) *v.* ALIZARIN.
ALIZARIN W S POWDER (M.) *v.* ALIZARIN RED S (B.).
ALIZARIN X (By.) *v.* FLAVOPURPURIN.
ALIZARIN AZO YELLOW (H.). 1898. An acid mordant dye, giving an olive yellow with chrome mordant.
ALIZARIN BLACK BLUE (By.) *v.* ALIZARIN CYANINE BLACK (By.).
ALIZARIN BLACK P (M.). An anthracene derivative. *Trioxyanthraquinone quinoline.* The quinoline of flavopurpurin:

$$C_6H_3(OH) \big<{}^{CO}_{CO}\big> C_6 \big<{}^{(OH)_2}_{C_3H_3N}$$
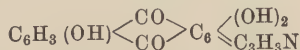
(Alizarin blue is the quinoline of alizarin). 1890. Greenish-black paste insoluble in water, soluble in caustic alkali, giving a strongly coloured, dirty green solution. In concentrated H_2SO_4 dirty reddish-brown solution, brown ppt. on dilution.

Application. — A mordant dye. Dyes chrome-mordanted *wool* or *cotton* violet-grey to black. Used also in calico printing in conjunction with chromium acetate.

ALIZARIN BLACK S (M.). *Bisulphite of soda compound of Alizarin black P* (M.). Dark brown paste soluble in water with a brown colour. Alkaline solution black-violet. Concentrated H_2SO_4, brown solution, which ppts. on dilution.

Application. — A mordant dye. Dyes chrome-mordanted *wool* or *cotton* grey to black. Principally used in calico printing.

ALIZARIN BLACK S PASTE (B.). *Alizarin black S W paste* (B.), *Alizarin blue black S W* (B.), *Naphthazarin S. Sodium bisulphite compound of dioxynaphthoquinone.* Naphthazarin (dioxynaphthoquinone) is the "alizarin" of naphthalene, produced by the action of zinc and concentrated H_2SO_4 on dinitronaphthalene :

$$C_{10}H_4O_2(OH)_2.$$
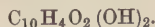
Naphthazarin. 1861. Alizarin black S paste. 1887.
Properties. — Black paste, soluble in boiling

water with a reddish-brown colour. In alcohol, yellowish-brown solution with green fluorescence. Alkaline solution bright blue. Conc. H_2SO_4, dull yellowish-green solution becoming red on boiling with evolution of sulphurous acid. On dilution, brown solution with black ppt.

Application. — A mordant dye. Dyes chrome-mordanted *wool* black. Used also in *calico* printing in conjunction with chrome mordant.

ALIZARIN BLUE PASTE (B.). *Alizarin blue A, D N W, F, R, R R* (M.); *Alizarin blue R, G W* (By.); *Alizarin blue A B* (B.A.Co.). An anthracene derivative. *Dioxyanthraquinone quinoline.* The quinoline of alizarin. 1877.

$$C_6H_4 \big<{}^{CO}_{CO}\big> C_6 \big<{}^{(OH)_2}_{C_3H_3N}$$
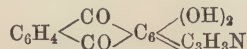
Produced by action of concentrated H_2SO_4 and glycerin at 90° C. on beta-nitroalizarin (alizarin orange).

Properties. — Dark blue glistening crystals or dark blue paste. Insoluble in water or cold alcohol, but slightly soluble in boiling alcohol with a blue solution. In concentrated H_2SO_4 carmine-red solution, becoming yellowish-red on dilution with water. Forms a lime lake, insoluble in water, the presence of acetic acid preventing its formation. Alizarin blue contains the two hydroxyl groups of alizarin, and is therefore a weak acid, forming lakes with metallic bases. With *calcium, barium, zinc,* and *iron,* greenish-blue lakes are produced; with *chromium* and *nickel,* blue lakes; with *aluminium,* purplish-blue; and with *tin,* purple. Being a derivative of quinoline it also possesses basic properties, combining with acids to form unstable salts. It is reduced by alkaline reducing agents, forming a red solution which is re-oxidised to blue on exposure to air. It may thus be applied in a vat similarly to indigo.

Application. — The vat-dyeing process just mentioned has not proved a practical success. Alizarin blue is not applied in *cotton* dyeing, but is used in *wool* dyeing in conjunction with chrome mordant, with which it produces indigo blue shades. On account of its insolubility alizarin blue possesses little penetrative power, and is apt to dye irregularly, but is improved in these respects by adding bisulphite of soda solution. Alizarin blue S is, however, more frequently employed.

ALIZARIN BLUE A (M.).
ALIZARIN BLUE A B (B.A.Co.)
ALIZARIN BLUE D N W (M.).
ALIZARIN BLUE F (M.).
ALIZARIN BLUE G W (By.).
ALIZARIN BLUE R (M.) (By.).
ALIZARIN BLUE R R (M.).
    v. ALIZARIN BLUE PASTE.

ALIZARIN BLUE S POWDER or PASTE (B.). *Alizarin blue soluble powder*

(B.A.Co.), *Alizarin blue S. Sodium bisul-phite compound of alizarin blue.* 1881.

$$C_6H_4 <^{C(OH)SO_3Na}_{C(OH)SO_3Na} > C_6 <^{(OH)_2}_{C_3H_3N}$$
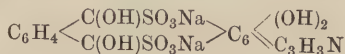
Obtained by the action of concentrated bisul-phite solution on alizarin blue for two or three weeks.

Properties.—Chocolate-brown powder or paste. Easily soluble in water with yellowish-brown colour. Insoluble in alcohol. In con-centrated H_2SO_4, dark yellow solution, brown ppt. on dilution. The aqueous solution is resolved into insoluble alizarin blue and sodium bisulphite on heating to 70° C.

Application.—Since alizarin blue S decom-poses as stated above when its solution is heated to about 70° C., the dyestuff must be dissolved at a low temperature, and the dye bath must not be raised above 65° C. until the colouring matter has been well taken up by the fibre. Most of the colouring matter is absorbed between 55° and 65° C., and when the bisulphite compound is decomposed, the regenerated insoluble alizarin blue gradually combines with the mordant on the fibre with formation of the insoluble colour lake. *Cotton dyeing.*—(*a*) Mordant with chromium (see MORDANTS), dye with alizarin blue S with-out calcium acetate; (*b*) Pad in a solution con-taining alizarin blue S and chromium acetate, dry at a low temperature, and steam. Aliz-arin blue S dyed as above produces navy-blue shades on cotton, which are very fast to light and all other influences, but it is not greatly used on account of its high cost. *Wool dyeing.*—Alizarin blue S is a valuable substi-tute for vat indigo on wool. Unlike the latter, it does not require any special process for its application, and, moreover, the dyed colour has not the defect of rubbing off. It is also very fast to milling; but although extremely permanent to light, is slightly in-ferior to indigo in this respect. It does not show the purplish bloom of vat indigo, which may, however, be imitated by topping after dyeing with alizarin cyanine 2 R (By.), or other suitable dye. This dyestuff is used only in conjunction with chromium mordant; bichromate of potash, and tartar or lactic acids being not satisfactory. The dyeing takes place in a separate bath, the solution being raised very slowly to 65° C., maintained at that temperature until well exhausted, then raised to the boil, and the boiling con-tinued for one or two hours. Calcareous water must be neutralised with acetic acid. *Silk dyeing.*—Very fast navy-blues are ob-tained with alizarin blue S on chrome mordant.

ALIZARIN BLUE S N G, S N W, S W N (B.) These colours are either identical or isomeric with the ANTHRACENE BLUES (B.) (*q.v.*).

ALIZARIN BLUE BLACK S W (B.) *v.* ALIZARIN BLACK S (B.).

ALIZARIN BORDEAUX B (By.). *Aliz-arin bordeaux B D* (By.). An anthracene derivative. *Tetroxyanthraquinone (quinaliz-arin).*

$$C_6H_2(OH)_2 <^{CO}_{CO} > C_6H_2(OH)_2$$
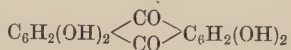
1890. Produced by the action of fuming H_2SO_4 (70 per cent. anhydride) at 170° C., on alizarin.

Properties.—A brownish-red paste. Insol-uble in water, but soluble in dilute caustic soda with reddish-violet colour. In concen-trated H_2SO_4, blue-violet solution, brownish-red ppt. on dilution.

Application.—A mordant dye similar in properties to alizarin, but producing with the various mordants much bluer shades than the latter. *Cotton dyeing.*—Alizarin bordeaux produces bright and fast bluish-claret shades with alum mordant by the Turkey-red process. With chromium mor-dant it yields violet-blue shades. *Wool dyeing.*—Alizarin bordeaux B gives bright bluish-violet shades with chrome mordant, these being bright and very fast to light, milling, &c. Chromic salts are preferable to bichromate since brighter colours are thereby produced, and either the "two bath" or "single bath" process may be employed. A long boiling is necessary to completely develop the colour.

ALIZARIN BORDEAUX G and G G (By.). Isomeric with alizarin bordeaux B, probably

$$C_6H_3(OH) <^{CO}_{CO} > C_6H(OH)_3$$
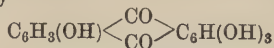
Mark G gives the same reactions as mark B, but G G, with sulphuric acid, produces a bluish-red solution which on dilution becomes redder and then gives a brown ppt.

ALIZARIN BROWN (P). *Alpha-nitro-alizarin* is sometimes sold under this name. It produces yellowish-browns with chrome mordant, but is little used.

ALIZARIN BROWN *v.* ANTHRACENE BROWN.

ALIZARIN CARDINAL (By.). *Alizarin granat R* (M.). An anthracene derivative. *Alpha-amidoalizarin,*

$$C_6H_4 <^{CO}_{CO} > C_6H <^{(OH)_2}_{NH_2}$$
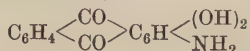
1877. Reduction of alpha-nitroalizarin. Car-mine-red or red-brown paste. Insoluble in water. Soluble in alcohol, with carmine-red colour. In concentrated H_2SO_4, brown solu-tion, carmine-red on dilution.

Application.—Produces a bluish-red shade with alum mordant. Used in *calico* printing and *wool* dyeing.

ALIZARIN CARMINE v. ALIZARIN RED S.

ALIZARIN CYANINE G (By.). An anthracene derivative. Constitution uncertain; probably an *imide of tri-* or *tetra-oxyanthradiquinone*. Produced by the action of ammonia upon an intermediate product formed in the oxidation of alizarin bordeaux into alizarin cyanine R. 1890. Black paste insoluble in water. In alcohol blue-violet solution. In dilute NaOH, greenish-blue solution. In concentrated H_2SO_4, red solution, which gives a black ppt. on dilution. On long boiling with dilute caustic soda it loses ammonia, and is converted into alizarin bordeaux.

Application.—A mordant dye. *Cotton.*— With chromium mordant very green shades of blue are produced, and with alum dark blue. On *wool* it is used only with chrome mordant, and gives greenish-blues which are very fast to light, milling, &c. The water should be free from lime salts, or neutralised with acetic acid. The alizarin cyanines are superior to alizarin blue in respect of fastness to milling, particularly in pale shades.

ALIZARIN CYANINE R (By.). An anthracene derivative. A *penta oxyanthraquinone* of the constitution

$$C_6H_2(OH)_2 <^{CO}_{CO}> C_6H(OH)_3$$
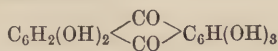
1890. Obtained by heating alizarin bordeaux with sulphuric acid and manganese dioxide or arsenic acid. Dark-brown paste insoluble in water. Soluble in alcohol with a dark-brown colour. Soluble in dilute NaOH with a blue colour, and in concentrated H_2SO_4 gives a blue solution with a red fluorescence, which is pptd. as brown flocks on dilution.

Application.—As alizarin cyanine G, but produces indigo-blue with chrome mordant instead of greenish-blue shades.

ALIZARIN CYANINE 2 R (By.) and **R A** (By.). Constitution not published.

ALIZARIN CYANINE 3 R (By.). Obtained by the action of H_2SO_4 containing 70 per cent. anhydride at 35° to 40° C. on alizarin. The sulphuric ether which is formed (and from which cyanine G is produced) is saponified by heating with dilute acid.

Application.—Similar to that of the other alizarin cyanines, but gives very red shades.

ALIZARIN CYANINE N S (By.) gives a greenish-blue shade.

The various *Alizarin cyanine powders*, which are soluble in water, are the sodium salts of the various alizarin cyanine pastes.

ALIZARIN DARK BLUE (B.). Dirty-green paste, soluble in hot water with greyish-green colour. Slightly soluble in alcohol with reddish-brown colour. Concentrated H_2SO_4 gives reddish-brown colour, which becomes redder on dilution.

Application. — A mordant dye. Gives indigo-blue shade on chrome mordanted *wool*.

ALIZARIN DARK GREEN W (B.). 1898. A mordant dye, producing bluish-green shades on chrome mordanted *wool*.

ALIZARIN GRANAT R (M.) v. ALIZARIN CARDINAL (By.).

ALIZARIN GREEN v. COËRULEÏN.

ALIZARIN GREEN B (D.). An oxazine derivative. Action of *beta-naphthoquinone sulphonic acid* on *amidonaphthol sulphonic acid*,

$$C_{10}H_4 <^{(OH)_2}_{<^O_N}> C_{10}H_5 . SO_3H$$
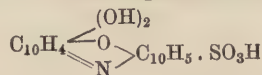
1895. Black-green powder soluble in water with a green colour. In concentrated H_2SO_4, dirty blue-violet solution, changing to yellow-green, and finally giving a red ppt. on dilution.

Application.—A mordant dye, giving a green colour on *wool* or *cotton* mordanted with chrome.

ALIZARIN GREEN G (D.). An oxazine derivative. Isomeric with the above. 1895. Brown-black powder, soluble in hot water with greyish-green colour. In concentrated H_2SO_4, bluish-green solution; on dilution becomes green, then violet, and finally ppts. as red flocks.

ALIZARIN GREEN S (M.). An anthracene derivative. Bisulphite of soda compound of *alpha-alizarin quinoline*,

$$C_6H_4 <^{CO}_{CO}> C_6 <^{(OH)_2}_{C_2H_3N} + NaHSO_3$$
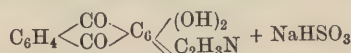
Isomeric with alizarin blue S. 1892. Obtained by action of glycerin, nitrobenzol, and concentrated H_2SO_4, an alpha-amidoalizarin (alizarin granat), and treatment of the product with sodium bisulphite. Bluish-red crystalline paste or powder, slightly soluble in water with a red-violet colour. Insoluble in alcohol. Carmine-red solution in alkali. In concentrated H_2SO_4, cherry-red solution. On treatment with alkaline reducing agents readily forms a reduction product, which re-oxidises in the air. A vat may thus be produced.

Application.—A mordant dye. Produces a light bluish-green on *cotton* or *wool* mordanted with chrome. Principally used in *calico* printing with a nickel-magnesium mordant, with which it gives a beautiful green.

ALIZARIN GREEN S (B.). *Mixture of sodium bisulphite compounds of tri-* and *tetra-oxyanthraquinone quinoline and their sulphonic acids* chiefly:

$$C_6H_2(OH)_2 <^{C . OH . SO_3Na}_{C . OH . SO_3Na} > C_6 <^{(OH)_2}_{C_3H_3N}$$
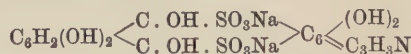
1888. Action of concentrated H_2SO_4 on alizarin blue and treatment of the product with sodium

bisulphite. Brownish-black solution soluble in cold water, on boiling insoluble alizarin green separates out. In alkalies, blue solution. In concentrated H_2SO_4 dissolves with a violet colour, which gives a brown ppt. on dilution.

Application.—A mordant dye. Produces dull greenish-blues on *cotton* or *wool* mordanted with chrome. Principally used in *calico* printing with chromium acetate or bisulphite as mordant. The colours are very fast to light and (on wool) to milling.

ALIZARIN HELIOTROPE R (By.). 1899. A mordant-dye. Dyes unmordanted *wool* from an acid bath bluish - red, chrome-mordanted *wool* bluish - violet. Specially suited for *calico* printing, producing reddish-violet shades with alumina mordant.

ALIZARIN INDIGO-BLUE S (B.). An anthracene derivative. *Sodium bisulphite compound of penta- and tetra-oxyanthraquinone quinoline, with their sulphonic acids* chiefly:

$$C_6H(OH)_3 < {{C . OH . SO_3Na} \atop {C . OH . SO_3Na}} > C_6 < {{(OH)_2} \atop {C_3H_3N}}$$
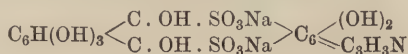
1888. Brownish-black paste, soluble in cold water, with red-brown solution, but, on boiling, insoluble alizarin indigo - blue separates out. Alkaline solution, blue. Concentrated H_2SO_4, blue solution, which gives a reddish-brown ppt. on dilution.

Application.—A mordant dye. Produces indigo - blue shades in conjunction with chrome mordant, and is used in exactly the same way as alizarin blue S.

ALIZARIN MAROON (B.). An anthracene derivative. *Mixture of alpha- and beta-amido alizarin and amidopurpurin.* 1885. Reduction product of nitro alizarin. Obtained by action of sulphuretted hydrogen on nitro alizarin in ammoniacal solution. Dark violet paste insoluble in water. Violet solution in alkali. In concentrated H_2SO_4, red solution, brown ppt. on dilution.

Application.—A mordant dye. Produces maroon shades with chrome, and garnet-red shades with alum mordant. Used in *wool*, *silk*, and *cotton* dyeing. The shades obtained are somewhat less fast than with alizarin red, &c.

ALIZARIN OIL *v.* TURKEY-RED OIL.

ALIZARIN ORANGE (B.). *Alizarin orange A* (B.).; *Alizarin orange G R and O G* (By.); *Alizarin orange N* (M.); *Alizarin orange A O* (B. A. Co.); *Nitro alizarin*; *Beta-nitro alizarin.* An anthracene derivative. 1876.

$$C_6H_2 < {{CO} \atop {CO}} > C_6H < {{(OH)_2} \atop {NH_2}}$$
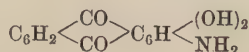
Produced by action of nitric acid on alizarin in suspension in ligroïn, acetic acid, or nitro-benzol. Brownish-yellow paste insoluble in water. Soluble in dilute alkalies with red colour, insoluble in concentrated alkalies. In concentrated H_2SO_4, yellowish-brown solution, which gives light yellow ppt. on dilution. On reducing the alkaline solution with zinc dust, it changes to a yellowish-brown colour, which turns blue on exposure to air.

Application.—A mordant dye. Very extensively used in *wool dyeing* as a substitute for madder, being somewhat cheaper than alizarin red when dyeing browns and other compound shades with chrome mordant. Although alizarin is the madder colouring matter, the natural dyestuff gives much browner shades than artificial alizarin, on account of impurities which are absorbed by the wool, hence nitroalizarin, which gives reddish-browns with *chrome* mordant, gives colours more nearly approaching those of madder than does alizarin itself. The bichromate mordant is preferable to chromic salts, but both may be employed either by the two-bath or single-bath method. Acetic acid should be added to calcareous water.

With *aluminium* mordant orange shades are obtained, and with *iron* purplish-browns; *copper* producing brownish-reds and stannic salts, oranges. *Stannous salts* reduce the colour to amidoalizarin (alizarin maroon), and the same action may take place if alizarin orange is mixed with any bisulphite alizarin colour, such as alizarin blue S, in concentrated solution

Alizarin orange produces very fast colours, the reddish-brown chromium shades being amongst the most permanent dyes known.

Cotton dyeing.—Little used, but employed in calico printing for the production of oranges with alum mordant.

ALIZARIN ORANGE POWDER (M.). *Alizarin orange A O P* (B. A. Co.). *Sodium salt of alizarin orange.* Brown powder soluble in water; reactions similar to those of alizarin orange. Applied also in a similar manner to the paste colour, but the bath is gradually acidified with acetic acid as the dyeing proceeds. Has four to five times the colouring power of the paste.

ALIZARIN POWDER S A *v.* ALIZARIN RED S.

ALIZARIN POWDER W *v.* ALIZARIN RED S.

ALIZARIN PUCE. Obtained in calico printing by using a mixture of aluminium and iron mordants with alizarin.

ALIZARIN RED S (B.). *Alizarin S ; Alizarin W S* (M.); *Alizarin powder W* (By.); *Alizarin powder S A* (B. A. Co.). *Alizarin carmine* (B. A. Co.). An anthracene derivative. *Sodium salt of alizarin monosulphonic acid.* 1878.

$$C_6H_4 < {{CO} \atop {CO}} > C_6H < {{(OH)_2} \atop {SO_3Na}}$$
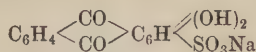
Obtained by the action of fuming H_2SO_4 on

alizarin.   Orange powder easily soluble in water.   NaOH, intense violet-coloured solution.   In concentrated H_2SO_4, brownish-yellow solution, which becomes yellow on dilution. Decomposes when strongly heated, alizarin being regenerated.

Application.—Mordant dye. *Cotton dyeing.* —Not used. *Wool dyeing.*—On account of its easy solution and great penetrative power, it is specially adapted for dyeing hard-twisted yarn or closely-felted material, or for use in mechanical dyeing machines, such as Obermaier's.   Produces with *chrome* mordants, maroon shades ; with *alum*, scarlet-red ; with *iron*, violet ; and with *tin*, bright orange.   Is from two to three times as strong as alizarin 20 per cent. paste.   May be dyed by the same processes as alizarin paste, and also as follows :—Boil first with the colour solution only, then gradually acidify with acetic acid, add the mordant solution, and boil for thirty to sixty minutes longer. Alizarin S produces shades which are fast to light, but which will not withstand milling.

ALIZARIN 2 S and 3 S (B.) are products similar to alizarin S, but derived from *flavo-* and *anthra-purpurin* respectively. They give yellower shades than the unsulphonated dyes, and are very little used.

ALIZARIN VIOLET *v.* GALLEÏN.   In *calico* printing and *cotton* dyeing the term is applied to the colour produced by alizarin red with iron mordant.

ALIZARIN VIRIDINE (By.).   A mordant dye.   Specially suitable for *calico* printing with acetate of chrome as mordant.

ALIZARIN YELLOWS.   Several of the so-called "alizarin" and "anthracene" yellows are not derivatives of those bodies, but are conveniently classed with the true alizarin dyes, on account of their similarity of application.

ALIZARIN YELLOW A (B.).   An oxyketone derivative. *Trioxybenzophenone.*

$$C_6H_5 - CO - C_6H_2(OH)_3$$
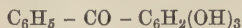
Condensation of benzoic acid with pyrogallol. 1889.   Greyish-yellow paste soluble in boiling water, soluble in NaOH to yellow solution, which quickly oxidises with formation of a green product.   In concentrated H_2SO_4, yellow solution, which yields a white ppt. on dilution.

Application.—A mordant dye.   Used only in *cotton* dyeing and printing in conjunction with aluminium mordant, with which it produces orange-yellow shades fairly fast to light and soap.

ALIZARIN YELLOW C (B.).   An oxyketone derivative. *Trioxyacetophenone* (*Gall-acetophenone*).

$$C_6H_3 . OH_2 . CO - CH_3$$

Condensation of acetic acid with pyrogallol

in presence of zinc chloride. 1881.   Greyish-white paste easily soluble in hot water. Soluble in dilute caustic soda solution with a brown colour, which becomes darker by oxidation on exposure to air.   In concentrated H_2SO_4, light yellow solution.

Application.—A mordant dye.   Used chiefly in *cotton* dyeing and printing with *aluminium* mordant, with which it gives greenish-yellow shades.   With *chromium* it produces greyish-brown, and with *iron* grey to black shades.

ALIZARIN YELLOW F S (D. & H.).   An azo compound. *Triamidodiphenyltolylcarbinol-triazosalicylic acid.* 1890.   Obtained by combining diazotised magenta with salicylic acid. Yellowish-brown paste insoluble in water. Dilute NaOH, orange-yellow solution ; concentrated H_2SO_4, green solution.

Application.—A mordant and an acid dye. Produces yellow shades fast to light and milling on *wool* mordanted with chrome.

ALIZARIN YELLOW G G PASTE (M.). *Alizarin yellow G G W powder* (M.).   Azo compounds.   The latter is the sodium salt of the former, which is *meta nitraniline azosalicylic acid.*

$$C_6H_3 . NO_2 . N : N - C_6H_2 . OH . COOH$$
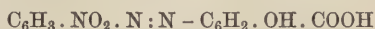
1887.   Yellow paste (G G) or powder (G G W), the former being insoluble, the latter soluble in water.   In NaOH, orange-yellow solution. Concentrated H_2SO_4, orange solution, yielding a bright yellow precipitate on dilution.

Application.—A mordant or an acid dye. *Wool*—largely used with chrome mordant, with which it gives greenish-yellow shades which are very fast to light and milling. May be combined with other alizarin colours and dyed either by two-bath or single-bath process.   With alum mordant it yields fugitive golden-yellow shades.   May also be applied as a simple acid colour, but with less useful results. *Cotton dyeing and calico printing.*—Good greenish-yellows with chrome mordant.

ALIZARIN YELLOW PASTE (M.).   This body is a natural product and not a coal-tar derivative.   Its synonym is *ellagic acid* (*q.v.*).

$$CH(OH)_3 . CO - C_6H(OH)_3 . COOH$$
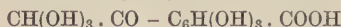
It is prepared by extracting dividivi or myrabolams with hot water, and decomposing the ellagitannic acid thus obtained with dilute acid.   Light brown paste insoluble in water.   In dilute NaOH, brown-yellow solution, which readily absorbs oxygen from the air.   In concentrated H_2SO_4, red-brown solution, from which the ellagic acid is precipitated by dilution.

Application.—A mordant dyestuff, giving drab-yellow shades on chrome-mordanted *wool*.   Not used for *cotton*.

ALIZARIN YELLOW R (M.) (By.) (C.R.). *Terra cotta R* (G.) ; *Orange R* (Culoz.).   An

azo colour. *Paranitranilineazosalicylic acid.*
Alizarin yellow R W (M.). Sodium salt of
same.

$$C_6H_4 . NO_2 . N : N - C_6H_3 . OH . COOH$$
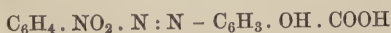
1885. Light brown paste (R), or brownish-
yellow powder (R W); the former insoluble,
the latter soluble in water. Soluble in NaOH
with a blood-red colour. In concentrated
H_2SO_4, orange-yellow solution, brownish-
yellow ppt. on dilution.
Application.—A mordant and an acid dye.
Use and properties same as alizarin yellow
G G. Gives full brown-orange shade on
chromium mordant.

ALIZARIN YELLOW W (B.). An oxy-
ketone derivative. Obtained by condensation
of *alpha-naphthol* with *gallic acid in presence
of zinc chloride.* 1890.

$$C_6H_2(OH)_3 - CO - C_{10}H_6 . OH$$

Application. — A mordant dye. Dyes
chrome-mordanted *wool* yellow.

ALKALI. In a general sense, the term
alkali is applied somewhat vaguely to a
number of substances possessing certain pro-
perties in common. They are soluble in
water, and saturate and neutralise acids
completely. The term is usually applied
both to the hydrates (caustic alkalies) and to
the carbonates (mild alkalies) of potassium,
sodium, lithium, and ammonium. Com-
mercially, the term alkali without any quali-
fication is generally understood to refer
exclusively to sodium carbonate. 58 per
cent. alkali is nearly pure sodium carbonate,
the 58 referring to the percentage of Na_2O
present.

ALKALIMETRY *v.* ACIDIMETRY.

ALKALINE CHROME MORDANT *v.*
CHROMIUM (*Chromium acetates*).

ALKALINE IRON MORDANTS *v.* IRON
(*Ferric salts*).

ALKALINE PINK MORDANT *v.* ALU-
MINIUM (*Aluminate of soda*).

ALKALI BLUE. *Nicholson's blue.
Guernsey blue.* Made and sold by almost all
colour manufacturers. A triphenylmethane
derivative. *Mixture of sodium salts of tri-
phenylrosaniline monosulphonic acid and tri-
phenylpararosaniline monosulphonic acid.* Ros-
aniline derivative :

$$\begin{matrix} OH \\ C_6H_4 \\ SO_3Na \end{matrix} . NH . C_6H_4 > C < \begin{matrix} C_6H_3 . NH . C_6H_5 \\ CH_3 \\ C_6H_4 . NH . C_6H_5 \end{matrix}$$
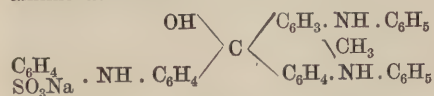
1862. Obtained by action of sulphuric acid on
insoluble spirit blue. The various shades of
alkali blue, represented by the letters R, 2 R,
B, 2 B, &c., and which range from purplish to
greenish-blue, correspond to different degrees
of purity of the original spirit blue. The
pure blue or greenish-blue shades, being most

highly purified, are most costly. Light or
dark blue powder, sparingly soluble in cold,
easily in hot water, with a pale blue colour.
Insoluble in dilute acid. Soluble in NaOH
with reddish-brown colour. In concentrated
H_2SO_4, brownish-red solution, which becomes
blue and precipitates on dilution.
Application.—An acid dye. *Cotton dye-
ing.*—Not used. *Wool dyeing.*—Dye in a neu-
tral or slightly alkaline (carbonate of soda,
borax, or sodium silicate) solution at the boil,
rinse, and develop in a cold (sulphuric) acid
solution. In the dye-bath the dye is fixed as
a colourless sodium salt, the colour being
developed by liberation of the free sulphonic
acid in the second bath. The colour cannot
be dyed direct from an acid solution because
the free colour-acid is insoluble.

Alkali blue yields reddish to greenish-blue
shades, which are superior to the soluble
blues in purity of shade and fastness to light
and milling; the latter process certainly
decolourises alkali blue, but the colour is
re-developed by acid. *Silk dyeing.*—Process
as for wool.

ALKALI BLUE 6 B (S.C.I.). *Methyl-
alkali blue.* A triphenylmethane derivative.
*Sodium salt of triphenylpararosaniline mono-
sulphonic acid,*

$$(C_6H_4 . NH . C_6H_4 . \begin{matrix} OH \\ SO_3Na) \end{matrix} > C < \begin{matrix} C_6H_4 . NH . C_6H_5 \\ C_6H_4 . NH . C_6H_5 \end{matrix}$$
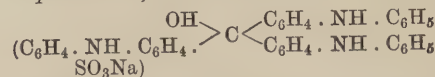
Obtained by the sulphonation of pure tri-
phenylpararosaniline—the latter prepared by
phenylation of pararosaniline. Dark blue
powder ; reactions same as alkali blue.
Application.—See ALKALI BLUE. Produces
purer shades of blue than ordinary alkali
blue.

ALKALI BLUE D (Ber.). Identical with
above, but prepared by sulphonation of tri-
phenylpararosaniline, prepared by action of
oxalic acid on diphenylamine. Reactions
and application as above.

ALKALI BLUE X G (Br., S. & Sp.). *Sol-
uble blue X G* (Br., S. & Sp.), *Non-mordant
cotton blue* (Br., S. & Sp.). A triphenyl-
methane derivative. *Sodium salt of sulphonic
acids of beta-naphthylrosaniline.* 1883. Grey-
ish-black lumps soluble in water with green
colour. In dilute NaOH violet-black solution
which entirely precipitates on heating. In
concentrated H_2SO_4, reddish-brown solution,
blue ppt. on dilution.
Application.—As ordinary alkali blues, but
dyes a greener shade.

ALKALI BROWN (D.). *Benzo brown
5 R* (By.). An azo compound. *Sodium salt of
primuline azophenylene diamine.* 1887. Dark
brown powder, soluble in water with a red
colour and in alcohol with a brown colour.
In concentrated H_2SO_4, bluish-violet solution
which gives a brownish-red ppt. on dilution.

Application.—A direct *cotton* dye. Dyes unmordanted cotton a reddish-brown from an alkaline bath.

ALKALI FAST RED B and R (M.). Reddish-brown powder (B.) and brown powder (R.). Soluble in water or alcohol with claret-red colour. Concentrated H_2SO_4, reddish-brown colour with evolution of HCl. On dilution changes to claret-red.

Application.—Acid colours, dyeing *wool* bluish-red shades, fast to alkali.

ALKALI GREEN (Br., S. & Sp.). *Viridine.* A triphenylmethane derivative. *Sodium salt of diphenyldiamidotriphenylcarbinol sulphonic acid.* 1877. Dark green powder, soluble in water with a green colour. In NaOH, brown solution. In concentrated H_2SO_4, magenta-red solution, green ppt. on dilution.

Application.—An acid dye. Now very little used. Dyes *wool* and *silk* bright green from an acid bath.

ALKALI RED (D.). A tetrazo compound.

$$Benzidine\begin{cases} Naphthionic\ acid.\\ Alpha\text{-}naphthylamine\\ \quad disulphonic\ acid. \end{cases}$$

Red powder, giving red solution in water. Slightly soluble in alcohol. In NaOH, red solution. In concentrated H_2SO_4, blue solution, purple ppt. on dilution.

Application.—A direct *cotton* dye. Dyes unmordanted cotton red from a salt bath.

ALKALI VIOLET (B.) (S. C. I.). A rosaniline derivative. *Sodium salt of tetraethylmono methylphenylpararosaniline monosulphonic acid.* 1886. Blue-violet powder soluble in water. In concentrated H_2SO_4, yellowish-red solution; on dilution, dirty green ppt., changing to blue.

Application.—An acid dye. *Wool dyeing.* —May be applied in alkaline, neutral or acid bath (best by alkali blue process) producing shades which are fast to milling. Used in conjunction with acid green or patent blue for production of indigo blue shades. *Silk dyeing.*—Applied as in *wool* dyeing, but preferably in a bath containing " boiled-off liquor " and sulphuric acid. *Cotton dyeing.* —Dyed on *cotton* prepared with tannin and tartar emetic. Shades moderately fast.

ALKALI VIOLET R (By.). Is probably closely allied to ALKALI VIOLET (B.).

ALKALI YELLOW (D.). *Oriol* (G.), *Cotton yellow R* (B.). An azo compound. *Primuline-azo-salicylic acid.* Reddish powder. In water orange-yellow solution. In H_2SO_4, scarlet coloured solution, brownish-yellow ppt. on dilution. Like other salicylic acid derivatives, forms lakes with metallic oxides, but these are duller in colour than the dye itself.

Application.—A direct *cotton* dye. Dyes unmordanted *cotton* reddish-yellow from an alkali bath containing salt. The colour is fairly fast to soap but not to light; unaffected by dilute acids, but reddened by alkalies.

ALKALI YELLOW R (D.). An azo compound.

$$Benzidine\begin{cases} Salicylic\ acid.\\ Dihydro\ thioparatoluidine\\ \quad sulphonic\ acid. \end{cases}$$

1889. Brownish-yellow powder, giving an opalescent yellow solution in water. In concentrated H_2SO_4, brownish-red solution.

Application.—A direct cotton dye. Dyes unmordanted *cotton* yellow from a soap bath.

ALKANET. The root of the *Anchusa tinctoria.* It contains a purple colouring matter, *anchusin*, which can be used on *wool* or *silk*; but it is now employed mainly in pharmacy to colour medicines, oils, pomades, &c., and in colouring beverages. The true colouring matter in red wines is " Ænolin," which has very similar properties to *anchusin*, but it is also stated that some wines contain a blue colouring matter identical with the *cyanin* of flowers.

ALPACA *v.* WOOL.

ALPHA - NAPHTHOL ORANGE *v.* ORANGE I.

ALPINE BLUE (G.). *Fast wool blue* (G.). A triphenylmethane derivative. *Sodium salt of tetramethylethylbenzyltriamidotriphenylcarbinol trisulphonic acid.* 1891. Dark violet powder, giving a blue solution in water or in alcohol. In concentrated H_2SO_4, green solution, which becomes blue on dilution.

Application.—An acid dye. Dyes *wool* and *silk* blue from an acid bath, the colour being fast to alkalies.

AL ROOT *v.* CHAY ROOT.

ALSACE GREEN *v.* DARK GREEN (B.)

ALUM *v.* ALUMINIUM SALTS.

ALUMINATES *v.* ALUMINIUM SALTS.

ALUMINIUM, Al. Atomic weight = 27·1. Next to oxygen and silicon, aluminium is the most widely distributed element in nature. Its oxide alumina, Al_2O_3, is found in a pure state as *corundum*, in a less pure condition as *sapphire, ruby, emery,* &c. Although there are many other compounds of aluminium found in nature, such as aluminates, basic sulphates, fluorides, phosphates, borates, &c., it occurs principally in the form of silicates, of which there are a very great number. Aluminium is obtained by heating to redness in a reverberatory furnace the double chloride of aluminium and sodium with metallic sodium. Aluminium is now also obtained by means of the electric furnace. Pure aluminium, obtained by heating the bromide with sodium, is a perfectly white metal, but as produced commercially it has a bluish tinge, which becomes intensified when the metal is worked and when much silicon and iron are present. Cast aluminium has a

specific gravity of 2·56, which may be increased by rolling to 2·688. The pure metal melts, according to Pictet, at 600° C. ; commercial aluminium, according to Castner, melts at about 700°, and appears to be quite non-volatile. When heated in air, especially at a white heat, aluminium oxidises ; in the presence of much silicon it burns brilliantly, ultimately forming silicate of aluminium. In thin foil the metal burns readily in air. The action of air, of water, and of dilute acids depends to a great extent upon the purity of the metal. Pure aluminium is not affected by air, moisture, or sulphuretted hydrogen. Commercial aluminium is rapidly oxidised by steam at high temperatures. Dilute sulphuric acid has little or no action, even in the presence of other metals. Cold concentrated sulphuric acid has very little action, but, on heating, the metal dissolves rapidly, and sulphur dioxide is evolved. Cold nitric acid, either strong or diluted, has practically no action and, on heating, the metal dissolves but slowly. Hydrochloric acid, on the other hand, dilute or concentrated, dissolves the metal readily, more rapidly if the metal is impure. Aluminium is very little affected by organic acids and, since the salts of aluminium are quite harmless, the metal is strongly recommended for vessels used for culinary purposes in place of tin and copper. Caustic alkalies readily dissolve aluminium with formation of aluminates and evolution of hydrogen. Aluminium is a trivalent element. The formulæ of its compounds, however, are usually written with two atoms of aluminium, $Al_2(OH)_6$, Al_2Cl_6, instead of the simple formulæ $Al(OH)_3$ and $AlCl_3$ respectively. According to vapour density determinations of the molecular weights of aluminium chloride and bromide, the double formulæ are correct. On the other hand, however, organo-metallic compounds of aluminium exist, the molecular weights of which prove the trivalent nature of the element. It is assumed, therefore, that the molecules Al_2Cl_6, Al_2Br_6, &c., are polymers of $AlCl_3$, $AlBr_3$, &c.

ALUMINIUM OXIDE, *Alumina*, Al_2O_3. This is the only known oxide of aluminium ; it is isomorphous with the sesquioxides of iron and chromium. As already indicated, it occurs native as *corundum, ruby, sapphire,* &c., in a crystalline form. Crystallised alumina may be obtained by strongly heating a mixture of aluminium fluoride and boron trioxide. Amorphous alumina is produced by heating the hydroxide. It is white and soft, but becomes hard on strong ignition. When prepared at a gentle heat, alumina is soluble in acids, but when strongly ignited it is rendered insoluble. It melts in the oxy-hydrogen blowpipe flame and crystallises with a density of about 4. In any form alumina is converted into soluble sodium aluminate by fusion with caustic soda, and into sulphate by fusion with potassium bisulphate.

Aluminium Hydroxides. — The normal hydroxide or hydrate, $Al_2(OH)_6$, occurs native as *hydrargillite.* It is produced in the form of a white translucent gelatinous precipitate on the addition of ammonium hydrate to a solution of an aluminium salt :—

$$Al_2Cl_6 + 6NH_4HO = Al_2(HO)_6 + 6NH_4Cl.$$
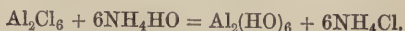
It loses water at 100° C., becoming soft and friable. When heated gently it is converted into the dihydrate $Al_2O_2(OH)_2$, which at a higher temperature becomes anhydrous. The dihydrate occurs associated with ferric oxide and silica in the important mineral *bauxite* from which aluminium sulphate, alum, and alumina are now largely manufactured. A hydrate of the composition $Al_2O(OH)_4$ is obtained by boiling the ordinary hydrate with water for twenty-four hours. By dialysis of a solution of aluminium hydrate in aluminium chloride, Graham obtained the hydrate $Al_2(OH)_6$ in a soluble form. This substance coagulates on heating, and is precipitated on the addition of acids, alkalies, or salts. Aluminium hydrate possesses both basic and acid properties. It forms *aluminium salts* with acids and *aluminates* with bases. The acid character of the hydrate is very feeble ; the aluminates are readily decomposed by all acids and by carbon dioxide with formation of aluminium hydrate. Alkaline carbonates, as well as hydrates, precipitate the trihydrate from solutions of aluminium salts. The presence of organic acids, as well as of sugar, glycerin, &c., prevent the precipitation. The precipitate at first formed with caustic soda or caustic potash redissolves on adding an excess of the alkali with formation of an aluminate. Excess of ammonia dissolves the precipitate slightly ; the solubility is much less in the presence of ammonium chloride or other ammonium salts. Caustic alkalies do not redissolve aluminium hydrate in the presence of magnesium salts. Advantage is taken of this property in certain cases of mordanting cotton with aluminium salts. Aluminium hydrate, freshly precipitated, attracts many inorganic and organic substances which are in the same liquid, either in suspension or solution, and on this account is useful in clarifying water, sugar solutions, &c. Many natural and artificial colouring matters are also attracted by aluminium hydrate and precipitated from their solutions, forming "colour lakes." It is in virtue of this property of forming "lakes" that aluminium hydrate acts as a mordant for colouring matters when fixed upon textile fibres.

Examination and Analysis of Aluminium Compounds. — The salts of aluminium are

colourless. Most of the ordinary salts are soluble in water, possess a sweetish astringent taste, and usually have a strongly acid reaction to litmus. On strong ignition the acid of soluble salts is volatilised, and alumina remains. Compounds of aluminium when heated, moistened with cobalt nitrate and again strongly heated, produce a fine sky-blue colour. Ammonium sulphide gives with solutions of aluminium a precipitate of aluminium hydrate, sulphuretted hydrogen being evolved. Barium carbonate causes the slow but complete precipitation of aluminium hydrate, with evolution of carbon dioxide. Sodium phosphate gives a bulky white precipitate of aluminium phosphate, soluble, like the hydrate, in caustic potash or soda, but insoluble in ammonium hydrate and ammonium chloride. It is soluble in dilute mineral acids, but not in acetic acid. Alkaline acetates precipitate aluminium phosphate from its solution in mineral acids. The presence of citric acid, but not tartaric acid or sugar, prevents its precipitation. Aluminium phosphate is soluble in solutions of other aluminium salts, and it is no doubt for this reason that sodium phosphate is not a good fixing agent for aluminium mordants on cotton. Sodium arseniate gives a white precipitate of aluminium arseniate, a reaction which is utilised in fixing aluminium mordants on the vegetable fibres. Sodium silicate added to solutions of aluminium salts does not form a silicate, but causes a precipitation of aluminium hydrate. The action of caustic alkalies and alkaline carbonates has been described above. Aluminium hydrate may be distinguished from gelatinous silica, which it closely resembles, by boiling with a drop or two of a weak solution of alizarin, when the hydrate assumes a bright red colour unaffected by the addition of a little dilute acetic acid. Aluminium is usually estimated by precipitating as hydrate, drying, igniting, and weighing as oxide (see ALUM). Salts of organic acids, such as the acetate (or any salts in the presence of organic matter), should be gently ignited and the residue dissolved in hydrochloric acid before proceeding with the precipitation. The estimation of alumina by Baeyer's method, which Sutton has found to give very fair technical results with alums and aluminium sulphate, may be very quickly performed. The method is based on the fact that if to a solution of alumina containing phenolphthaleïn normal soda is added in excess, or until the pink coloration is produced, normal acid being then added until the colour disappears, the volume of acid so required is less than the soda originally added in proportion to the quantity of alumina present. The difference between the volume of soda and acid used represents the amount of acid necessary to combine with the alumina set free by the alkali. The titration must take place in the cold and in dilute solutions. All salts of aluminium used in dyeing and calico-printing should be as free as possible from iron. (For the detection and estimation of iron, see ALUM, p. 32.)

ALUMINIUM SALTS. The salts of aluminium are, as a rule, easily soluble in water. They are colourless, and have a peculiar astringent taste. Even when containing no more acid than is necessary to saturate the metal, the alums are acid to litmus. Sulphuretted hydrogen produces no precipitate with aluminium salts, but ammonium sulphide causes a white precipitate of *aluminium hydrate*, hydrogen sulphide being liberated.

$$Al_2(SO_4)_3 + 3(NH_4)_2S + 6H_2O$$
$$= Al_2(OH)_6 + 3(NH_4)_2SO_4 + 3H_2S.$$
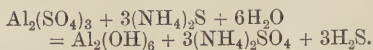
Phosphate of soda precipitates from solutions of aluminium salts, a white precipitate of *aluminium phosphate*.

$$Al_2(SO_4)_3 + 2Na_2HPO_4$$
$$= 2AlPO_4 + Na_2SO_4 + 2NaHSO_4$$

This voluminous precipitate is insoluble in acetic but dissolves in hydrochloric or nitric acid. Caustic soda also dissolves it, but ammonia does not. If the solution contains citric acid, the precipitate is not formed, but the presence of sugar or tartaric acid does not prevent it being thrown down. Aqueous solutions of aluminium salts dissolve aluminium phosphate. Liechti and Suida * find that one equivalent of aluminium sulphate $Al_2(SO_4)_3$ can keep one equivalent of aluminium phosphate, $AlPO_4$, in solution. This may account for the fact that sodium phosphate does not fix aluminium mordants readily. In contrast with the basic salts, aqueous solutions of normal aluminium salts are not decomposed by boiling or by diluting.

Sodium arseniate precipitates from the solutions of aluminium salts *aluminium arseniate* as a white powder, which is insoluble in water but soluble in acids. This reaction is used to fix aluminium mordants on the vegetable fibres.

Sodium silicate precipitates from the solutions of aluminium salts aluminium hydroxide; the silicic acid does not combine under these conditions with alumina; if the silicate of soda contains an excess of caustic soda, the precipitate of aluminium hydroxide may redissolve in the precipitant.

Basic Aluminium Salts.—Aluminium salts dissolve freshly-precipitated aluminium hydroxide, forming basic salts, as exemplified in the following equation :—

$$Al_2(SO_4)_3 + Al(OH)_3 = 3Al(SO_4)(OH).$$
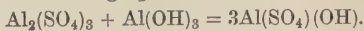
Basic salts are also obtained in a soluble form

* *Journ. Soc. Chem. Ind.*, 1883, p. 537.

by adding the requisite amount of the hydroxides or carbonates of potassium, sodium, ammonium, or calcium to the solutions of the normal salts, as shown by the following equations :—

$$Al_2(SO_4)_3 + 2NH_3 + 2H_2O$$
$$= 2Al(SO_4)(OH) + (NH_4)_2SO_4.$$

$$2Al_2(SO_4)_3 + 3Na_2CO_3 + 3H_2O$$
$$= Al_4(SO_4)_3(OH)_6 + 3Na_2SO_4 + 3CO_2.$$

$$Al_2(SO_4)_3 + 2CaCO_2 + 2H_2O$$
$$= Al_2(SO_4)(OH)_4 + 2CaSO_4 + 2CO_2.$$
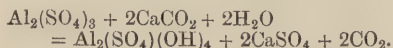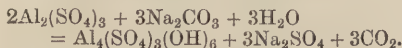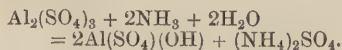
The solutions of the basic salts are more or less rapidly dissociated into normal salts and hydroxide, the latter being precipitated. For instance :—

$$3Al_2(SO_4)(OH)_4 = Al_2(SO_4)_3 + 2Al_2(OH)_6.$$
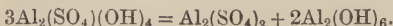
The dissociation is effected by heating or by dilution with water, and takes place the more readily the greater the basicity of the salt. The presence of other sulphates—e.g., sodium sulphate—in solution causes the basic salts to dissociate more readily. Probably still more basic sulphates than the compound $Al_2SO_4(OH)_4$ exist. These, however, are insoluble in water.

Aluminium Acetates.—The normal or triacetate of aluminium, $Al_2(C_2H_3O_2)_6$, has not been prepared in the solid state. A solution corresponding to this formula is largely made in various ways, but it is considered to consist of the diacetate and acetic acid. When a solution of the normal acetate is carefully evaporated to dryness, a residue is left having the composition $Al_2(C_2H_3O_2)_4(OH)_2$. A solution of the normal acetate may be obtained by dissolving aluminium hydrate in acetic acid, but it is generally prepared by mixing solutions of lead or calcium acetate with solutions of aluminium sulphate or alum. Lead acetate gives a purer product ; when calcium acetate is used, the solution always contains more or less calcium sulphate. With lead acetate and aluminium sulphate the reaction takes place according to the following equation :—

$$3Pb(C_2H_3O_2)_2 + Al_2(SO_4)_3$$
$$= 3PbSO_4 + Al_2(C_2H_3O_2)_6.$$
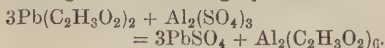
According to Liechti and Suida, normal aluminium acetate, in the absence of sulphates, is not dissociated either by boiling or by dilution with water. By adding various proportions of sodium carbonate to solutions of normal aluminium acetate, basic acetates of varying degrees of basicity are obtained. The following equations illustrate the formation of these basic acetates :—

$$2Al_2(C_2H_3O_2)_6 + Na_2CO_3 + H_2O$$
$$= 2Al_2(C_2H_3O_2)_5 \cdot OH + 2NaC_2H_3O_2 + CO_2.$$

$$2Al_2(C_2H_3O_2)_6 + 2Na_2CO_3 + 2H_2O$$
$$= 2Al_2(C_2H_3O_2)_4(OH)_2 + 4NaC_2H_3O_2 + 2CO_2.$$

$$2Al_2(C_2H_3O_2)_6 + 3Na_2CO_3 + 3H_2O$$
$$= 2Al_2(C_2H_3O_2)_3(OH)_3 + 6NaC_2H_3O_2 + 3CO_2.$$

$$2Al_2(C_2H_3O_2)_6 + 4Na_2CO_3 + 4H_2O$$
$$= 2Al_2(C_2H_3O_2)_2(OH)_4 + 8NaC_2H_3O_2 + 4CO_2.$$
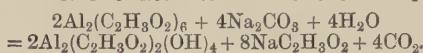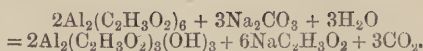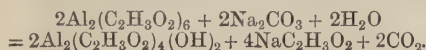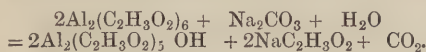
The formulæ in the second and fourth equations are doubled in order to show more clearly the progressive additions of sodium carbonate to form the more basic salts. The solution of basic acetates thus obtained—all of which, it will be observed, contain more or less sodium acetate—are dissociated on heating. The more basic the acetate, the lower is the temperature at which they dissociate. In the absence of alkaline sulphates no dissociation takes place at the ordinary temperature by dilution with water. The precipitates formed by heating solutions of basic acetates in the absence of sulphates do not redissolve when the liquid cools. In the presence of alkaline sulphates both the basic and normal aluminium acetates are dissociated by dilution with water, and dissociation takes place more readily by heating than in the absence of sulphates. The precipitates obtained by heating acetates containing sulphates redissolve on cooling. When aluminium acetate is prepared from alum instead of aluminium sulphate, the solution always contains a soluble sulphate, either potassium or ammonium sulphate :—

$$K_2Al_2(SO_4)_4 + 3Pb(C_2H_3O_2)_2$$
$$= Al_2(C_2H_3O_2)_6 + K_2SO_4 + 3PbSO_4.$$
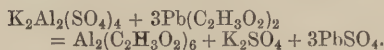
Basic acetates are usually prepared in the works by mixing solutions of aluminium sulphate, lead or calcium acetate, and sodium carbonate, thus :—

$$Al_2(SO_4)_3 + 2Pb(C_2H_3O_2)_2 + Na_2CO_3 + H_2O$$
$$= Al_2(C_2H_3O_2)_4(OH)_2 + Na_2SO_4 + 2PbSO_4$$
$$+ CO_2.$$
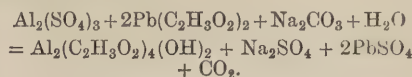
In both these cases a soluble sulphate is present, and the aluminium acetate, therefore, more readily dissociates. Lead sulphate is perceptibly soluble in aluminium acetate, and in certain cases where the presence of lead would prove injurious lead acetate is replaced by calcium acetate. Lead sulphate, however, is much less soluble in solutions containing sulphates such as in the above examples, and particularly when aluminium sulphate is also present.

Aluminium Sulphate Acetates. — For the formation of normal aluminium acetate 100 parts of aluminium sulphate require 171 parts of crystallised lead acetate, and 100 parts of potash or ammonia alum require 120 and 125 parts respectively. If a smaller proportion of lead acetate be used, sulphate acetates are produced. By adding also sodium carbonate or calcium carbonate the amount of lead acetate required to produce the mordant

liquor is still further reduced. Aluminium sulphate acetate may also be prepared by dissolving basic aluminium sulphate in acetic acid. The formation of some of the sulphate acetates prepared by Liechti and Suida is represented by the following equations :—

(1) $Al_2(SO_4)_3 + Pb(C_2H_3O_2)_2 = Al_2(SO_4)_2(C_2H_3O_2)_2 + PbSO_4.$

(2) $2Al_2(SO_4)_3 + 3Pb(C_2H_3O_2)_2 + Na_2CO_3 + H_2O = 2Al_2(SO_4)(C_2H_3O_2)_3OH + 3PbSO_4 + Na_2SO_4 + CO_2.$

(3) $Al_2(SO_4)_3 + Pb(C_2H_3O_2)_2 + Na_2CO_3 + H_2O = Al_2(SO_4)(C_2H_3O_2)_2(OH)_2 + PbSO_4 + Na_2SO_4 + CO_2.$

(4) $Al_2(SO_4)_3 + C_2H_4O_2 + 2Na_2CO_3 + H_2O = Al_2(SO_4)(C_2H_3O_2)(OH)_3 + 2Na_2SO_4 + 2CO_2.$
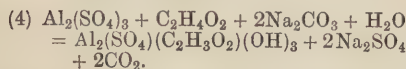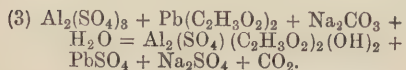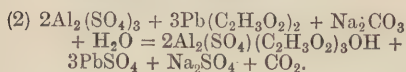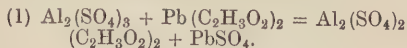
The first equation shows the formation of normal aluminium sulphate acetate. In all these cases, for the sake of simplicity, water of crystallisation in the aluminium sulphate and lead acetate has been omitted. The normal sulphate acetate does not dissociate when diluted with water, but it does when heated. The basic salts dissociate either when heated or when diluted, and the more basic are the salts the more readily do they dissociate. In all cases the precipitate produced by heating is gelatinous, and if the salt is not more basic than $Al_2SO_4(C_2H_3O_2)_3OH$ the precipitate is almost entirely redissolved on cooling. Aluminium sulphate acetates, both normal and basic, yield nearly the whole of their alumina to the fibre during mordanting, drying, and ageing. In this respect they are much stronger mordants than aluminium sulphates, and are about the same as the basic acetates. The investigations of Koechlin-Schoach and D. Koechlin have shown that in mordanting with sulphate acetates, basic aluminium sulphates, and not alumina, are fixed upon the fibre.

Red Liquor is a term applied both to aluminium acetates and aluminium sulphate acetates, normal and basic. The composition of these solutions varies greatly. They are usually prepared in practice by the double decomposition of aluminium sulphate and commercial acetate of lime, with or without soda or chalk. They have a yellowish-brown colour, due to the presence of empyreumatic substances derived from the calcium acetate. Their usual strength varies from specific gravity 1·08 to 1·12. Common red liquor is a crude sulphate acetate, whilst that known as *tin red liquor* consists for the most part of normal aluminium acetate. Hummel, in *Dyeing of Textile Fabrics*, gives the following examples as representative of innumerable recipés adopted in the manufacture of various red liquors :—

PARTS—GRMS., KILOS, OR LBS.

	Water.	Alum.	Aluminium Sulphate.	Lead Acetate.	Sodium Carbonate Cryst.	Chalk.	Calcium Acetate Solution. 1·12 sp. gr.
1	250	100	..	100	10	..	..
2	300	100	..	75	10	..	..
3	400	100	..	66·6	10	..	..
4	200	100	..	80	..	..	..
5	400	100	..	90	..	..	..
6	400	100	..	100	..	..	..
7	400	..	120	100	..	8·5	..
8	495	..	120	122·5	..	7·9	..
9	..	..	68	..	..	8	252
10	..	100	..	..	..	6	280

Uses. — Aluminium acetate and sulphate acetate in the form of "red liquor" are largely employed by the dyer and calico printer as mordants for the production of alizarin reds. They are of particular use in calico printing, and are applied in a variety of ways.

Examination and Analysis. — The best method of examining samples of red liquor is by means of comparative dye tests. For this purpose equal weights of cotton are impregnated with equal quantities of the samples to be examined and subsequently dyed with alizarin or some other mordant colour. The dyed material is then dried, and the colour of the swatches compared.

Estimation of Alumina.—About 5 grms. of the sample are evaporated to dryness in a platinum dish, and the residue gently ignited to destroy organic matter. When cold, the residue is dissolved in hydrochloric acid, and the alumina precipitated by ammonia, as described under ALUM (p. 32). Excess of aluminium sulphate must be looked for.

Estimation of Acetic Acid.—This is best performed by distillation with phosphoric acid, and titration of the distillate with $\frac{N}{1}$ soda and phenolphthaleïn, as described under CALCIUM ACETATE.

Aluminium Chloride Acetate, $AlCl(C_2H_3O_2)_2.$—This salt has been obtained from aluminium sulphate, lead acetate, and barium chloride solutions. It does not dissociate either on diluting or by heating. Liechti and Suida found that it yields to the cotton fibre only $3\frac{1}{4}$ per cent. of alumina after steeping, drying, and ageing.

Aluminium Nitrate Acetate, $Al(NO_3)(C_2H_3O_2)_2$, is obtained by the double decomposition of aluminium sulphate, with the acetate and nitrate of calcium or lead, and is used as a mordant for calico printing and silk dyeing. It is valuable for the production of fine steam alizarin reds, since it is very gradually dissociated on steaming.

Aluminium Chloride, $AlCl_3$. — When a current of chlorine is passed over a heated

mixture of charcoal and aluminium oxide, anhydrous aluminium chloride is produced.

$$Al_2O_3 + 3C + 3Cl_2 = 2AlCl_3 + 3CO.$$
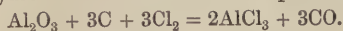
On the large scale it is manufactured by decomposing aluminium sulphate with calcium chloride. If aluminium hydrate be dissolved in hydrochloric acid, the resulting product contains water, which cannot be completely eliminated owing to partial decomposition of the aluminium chloride. It crystallises from the concentrated hydrochloric acid solution with six molecules of water. It combines readily with sodium chloride, &c., to form double salts — e.g., $AlCl_3$. NaCl.

The anhydrous salt, which forms white hexagonal tables, can be volatilised. It quickly absorbs moisture from the air and deliquesces. In moist air it decomposes, giving off fumes of hydrochloric acid. Aluminium chloride is sold in the form of a concentrated solution, which is not decomposed by diluting with water.

A number of basic aluminium chlorides have been prepared by Liechti and Suida.

The chlorides of aluminium yield very little alumina to the fibre, and attack vegetable fibres, consequently they are not suitable mordants. The use of aluminium chloride as a disinfectant has been suggested. It is made use of as a carbonising agent for destroying vegetable fibres in wool. The mixed material is placed in a solution of the normal chloride, the excess of liquid removed, and the material dried. The disintegrated vegetable fibres are removed as dust by shaking.

F. Breinl and E. Hanovsky * have shown that this salt is less suitable than magnesium chloride for carbonising purposes; or, at any rate, only equally suitable when it is absolutely devoid of free hydrochloric acid.

Their experiments prove that :—

1. A concentration of 10° Tw. for the aluminium chloride solution is sufficient to destroy all the vegetable fibres which may be present.

2. The solution used for carbonisation must be perfectly neutral, and must contain no free acid.

3. As regards the drying of the goods and the ventilation of the drying chamber, in case drying machines are not used, the same rules must be followed as mentioned for the carbonisation with magnesium chloride (q.v.). In consequence of the great instability of aluminium chloride these rules should be strictly adhered to.

4. The destruction of vegetable matters already begins at a temperature of 100° C., though it only goes on slowly, but higher temperatures turn the wool yellow.

* Journ. Soc. Dyers and Col., 1892, p. 208.

5. A complete removal of the aluminium chloride, after carbonising, by means of prolonged washing with water only—without the application of soda—is certainly possible, but a large quantity of water is necessary for the purpose.

Aluminium Hypochlorite, $Al(ClO)_3$.—This substance, which is generally known as *Wilson's Bleaching Liquor*, is prepared by mixing solutions of aluminium sulphate and chloride of lime. The mixture easily undergoes decomposition, oxygen being liberated and aluminium chloride being formed. Goods may be steeped in the diluted solution, which bleaches without the intervention of an acid. Its use as a mordant has also been suggested, as it decomposes on the fibre, aluminium hydrate being precipitated.

$$Al(ClO)_3 + 3H_2O = Al(OH)_3 + 3HOCl.$$

When used for bleaching and dyeing, the formation of aluminium chloride from the hypochlorite is a great disadvantage, as vegetable fibres are immediately attacked. It is used in paper-making, &c., where its antiseptic properties are of value.

Aluminium Nitrate, $Al(NO_3)_3 + 9H_2O$.— This salt is very soluble in water. It is formed by treating barium or lead nitrate with aluminium sulphate. It can also be prepared by dissolving aluminium hydrate in nitric acid. The crystals are deliquescent. When heated to 150° C. they are decomposed into nitric acid, aluminium oxide, and water.

Basic nitrates of aluminium are prepared by adding the requisite quantities of sodium carbonate to the solution of the normal salt; none of the nitrates are dissociated by heating or by dilution.

Aluminium nitrate is not employed as a mordant for silk or wool; it is used to some extent for producing steam colours on calico.

Aluminium Oxalate, $Al_2(C_2O_4)_3$.—On dissolving aluminium hydrate in oxalic acid and evaporating, an amorphous deliquescent mass remains. The mixture, which contains aluminium oxalate, is sometimes used in applying certain steam colours in calico printing. It is not used in silk or wool dyeing. The pure salt has not been prepared.

Aluminium Sulphate, $Al_2(SO_4)_3 + 18H_2O$. —Aluminium sulphate is prepared by dissolving aluminium oxide or hydroxide in sulphuric acid. On the large scale aluminium hydroxide (obtained from *cryolite*, $AlF_3 3NaF$), or *clay* (aluminium silicate), or *bauxite* (alumina containing ferric oxide), is dissolved in sulphuric acid, and the mass is evaporated until it solidifies on cooling.

Aluminium sulphate in the pure state forms monoclinic tablets, which contain 18 molecules of water of crystallisation, and dissolve very easily in water. In alcohol it is insoluble. The commercial article, known under the

names of *cake alum, patent alum*, and *concentrated alum*, occurs as a solid mass or irregular lumps, having a fused appearance. It often contains more than 55 per cent. $Al_2(SO_4)_3$, and should not contain less than 48 per cent.; the pure salt, $Al_2(SO_4)_3 + 18H_2O$, contains 51·35 per cent. $Al_2(SO_4)_3$. The article must be free from iron and from an excess of acid; the former injures the ultimate shade, while the latter is liable to weaken the vegetable fibres and to affect the reactions. It is not easy for the manufacturer to satisfy these demands; excellent qualities, however, are produced now which perfectly replace the more expensive alum; still aluminium sulphate should be carefully examined before use for *free acid*, *iron*, and percentage of $Al_2(SO_4)_3$, as its composition is very irregular, and varies even in different parts of the same piece.

Basic aluminium sulphates are obtained, as indicated above, by adding alkaline hydrates or carbonates, &c., usually sodium carbonate, to the solutions of aluminium sulphate (or alum). The greater the amount of alkali added, the greater is the basicity of the product, as shown by the following equations :—

(1) $Al_2(SO_4)_3 + Na_2CO_3 + H_2O$
     $= 2Al(SO_4)(OH) + Na_2SO_4 + CO_2.$

(2) $2Al_2(SO_4)_3 + 3Na_2CO_3 + 3H_2O$
     $= Al_4(SO_4)_3(OH)_6 + 3Na_2SO_4 + 3CO_2.$

(3) $Al_2(SO_4)_3 + 2Na_2CO_3 + 2H_2O$
     $= Al_2(SO_4)(OH)_4 + 2Na_2SO_4 + 2CO_2.$
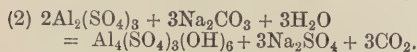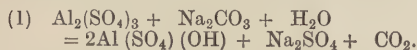
By the increase of basicity the intra-molecular cohesion is greatly diminished; the normal aluminium sulphate cannot be decomposed either by boiling or by diluting with water, the basic salt I. dissociates slowly and incompletely, salt II. more readily, and salt III. very quickly on boiling or diluting with water, separating gelatinous aluminium hydroxide, $Al_2(OH)_6$.

Liechti and Suida have tried to obtain pure basic sulphates by dissolving freshly-prepared aluminium hydroxide in a solution of the normal aluminium sulphate; they did not succeed, however, in obtaining very basic sulphates. On gradually adding aluminium hydroxide to the normal sulphate, sufficient to form the basic compound, $Al_2(SO_4)_3(OH)_6$, no alumina at all dissolved, and on filtering the solution was found to contain normal sulphate only, but no basic salt. It is supposed that the nascent basic compound becomes decomposed as follows :—

$$Al_4(SO_4)_3(OH)_6 = Al_2(SO_4)_3 + Al_2(OH)_6.$$

According to H. von Keler and G. Lunge * an aluminium sulphate used in Turkey-red dyeing should not contain more than 0·001 per cent. of iron. To produce a sulphate

* *Chem. News*, vol. lxx., p. 276.

more free from iron would be useless, since the influence of iron up to the above limit is quite trifling. But if this limit is exceeded, a minimal further addition of iron has a decidedly injurious effect. It does not here depend solely upon the total quantity of iron, but upon its state of oxidation. Ferrous salts are less hurtful than ferric compounds. The presence of zinc, which is certainly rarely detected in commercial aluminium sulphates, has an injurious effect upon the colour. In the choice of a sulphate it is, therefore, best always to select the sample poorest in iron and free from zinc.

A series of samples, in which the proportion of iron had been artificially raised to the abnormal quantity of 1 per cent., produced no injurious effect upon the shades of printing. This unexpected result may perhaps be explained by the consideration that in printing as compared with turkey-red dyeing only very slight quantities of mordant are applied to the fibre, whence the salts of iron are present in a quantity too trifling to affect the shades.

Some experiments were made with Persian berries, the yellow of which is regarded as of all printing colours the most sensitive to iron. Swatches printed with the smallest and highest proportions of iron (within permissible limits) showed no difference in the tone of the yellow, hence a proportion of iron in the aluminium sulphate up to 0·005 per cent. is unimportant in tissue printing. Aluminium sulphate is largely used in the manufacture of other aluminium mordants.

Analysis.—Aluminium sulphate in a pure state contains 15 per cent. of alumina, and may be examined in exactly the same manner as alum.

Free sulphuric acid is detected and estimated by a process recommended by Beilstein and Grosset * :—1 to 2 grms. are dissolved in 5 c.c. of water and 5 c.c. of a cold saturated solution of ammonium sulphate added. After fifteen minutes, 50 c.c. of 95 per cent. alcohol are added, and the whole filtered and washed with 50 c.c. of the same liquid. The alcoholic solution may then be examined for free acid, and the amount estimated by $\frac{N}{10}$ soda.

Aluminium sulphate crystallises with difficulty, and is more liable to contain impurities than alum. In many cases it is considered by dyers not to give such good results as common alum, and this may probably be due to irregular composition and to the absence of sulphate of potash or ammonia.

ALUM.—This name originally indicated the double sulphate of aluminium and potassium which crystallises in the shape of octahedra with 24 molecules of water of crystallisation.

* *Journ. Soc. Chem. Ind.*, 1890, p. 416.

The name has since been extended to a large class of compounds of analogous constitution and isomorphous form. They all possess the constitution $M_2R_2(SO_4)_4 . 24H_2O$ where M is a monatomic element or radicle, such as potassium, ammonium, sodium, &c., and R is one of the metals which form sesquioxides, such as aluminium, iron, and chromium. They all crystallise in octahedra with 24 molecules of water, and cannot be separated by crystallisation when present in solution together. A few of the more important alums are here enumerated :—

Potash alum, . $K_2Al_2(SO_4)_4,24H_2O$
Ammonia alum, $(NH_4)_2Al_2(SO_4)_4,24H_2O$
Soda alum, . $Na_2Al_2(SO_4)_4,24H_2O$
Chrome alum, . $K_2Cr_2(SO_4)_4,24H_2O$
Iron alum
(ferric ammonia) $\}$ $(NH_4)_2Fe_2(SO_4)_4,24H_2O$

The term "alum" without qualification refers to either potash or ammonia alum, whose properties for dyeing purposes are practically the same.

Potash Alum, $K_2Al_2(SO_4)_4,24H_2O$. — This salt occurs in nature as *kainite* as an efflorescence, or in fibrous crystals on aluminous minerals, occasionally as octahedra at Whitby, Campsie, &c. It occurs in larger quantities in various parts of Italy, also in Persia. The manufacture of alum is of great antiquity. It was employed as a mordant for dyeing bright colours in the time of Pliny. The greater portion of the alum manufactured in England was formerly obtained from alum shale, which occurs in large quantities at Whitby. *Alum shale* is a mineral consisting chiefly of aluminium silicate, iron pyrites, and bituminous substances. The shale, or ore, is piled up in large heaps and slowly roasted. At Whitby the ore is mixed with coal and brushwood, but at Campsie (Scotland) the mineral contains sufficient bituminous matter for its combustion, and, in fact, is usually mixed with spent rock to retard the calcination. The heaps are watered occasionally, and after exposure to the air for some months the soluble matter is extracted by lixiviation. During the roasting and exposure to air and moisture the iron pyrites is decomposed with the formation of ferrous sulphate, and free sulphuric acid which attacks the clay, forming aluminium sulphate. The solution subsequently obtained is freed from insoluble matter by subsidence and evaporated to the proper degree of concentration, when the requisite amount of potassium sulphate is added, and the alum allowed to crystallise. It is afterwards purified by recrystallisation. When ferric sulphate is present in any appreciable quantity in the crude liquor it is necessary to add sufficient potassium chloride to form the soluble salt ferric chloride, otherwise iron alum would crystallise out and

contaminate the product. At Top Tolfa, in Italy, alum has been prepared for many centuries from *alumite*, or *alum stone*, a mineral containing silicate and a basic sulphate of alumina and potash. Alum is now largely made in this country from sulphate of alumina obtained by treating *bauxite*, *cryolite*, or *alumite* with sulphuric acid.

Ammonia Alum, $(NH_4)_2Al_2(SO_4)_4,24H_2O$, occurs as *tschermigite* in Bohemia. The process of manufacture is practically the same as that of potash alum, substituting ammonium sulphate for potassium sulphate. It was first made on a large scale by Spence in 1845. He roasted the shale obtained from beneath the coal beds of South Lancashire for a period of about ten days in heaps piled upon loosely placed bricks, arranged so as to allow a free passage of air. The solution of aluminium sulphate subsequently obtained was treated either with gaseous ammonia or ammonium sulphate. By Spence's method the whole process occupied about a month, whereas the old process of manufacture as carried out at Whitby, Campsie, &c., extended over some twelve or fifteen months. At the present time ammonia alum, like potash alum, is largely obtained from aluminium sulphate produced by more direct means.

Properties.—Alum usually crystallises in octahedra, though when formed at the ordinary temperature in the presence of basic alum the crystals are cubes. For this reason *Roman alum* made from *alumite* (containing excess of alumina) is in the form of cubes. Alum possesses a sweetish astringent taste and a strongly acid reaction. The solubility of potash and ammonia alum in 100 parts of water at various temperatures is given in the following table (*Poggiale*) :—

Deg. C.	Parts of Potash Alum (Cryst.).	Parts of Ammonia Alum (Cryst.).
0	3·9	5·2
10	9·5	9·1
20	15·1	13·6
30	22·0	19·3
40	30·9	27·3
50	44·1	36·5
60	66·6	51·5
70	90·7	72·0
80	134·5	103·0
90	209·3	187·8
100	357·5	422·0

Alum is almost insoluble in a saturated solution of aluminium sulphate, and is quite insoluble in alcohol. Aqueous solutions of alum, unless very dilute, are not dissociated by boiling. By the addition of caustic alkalies or alkaline carbonates to solutions of alum so-called "neutral" and "basic" alums

are formed, which dissociate (forming precipitates of more basic salts) on boiling or on dilution with water. By carefully adding caustic soda to a solution of alum until the precipitate at first formed is just redissolved, a solution is obtained which has a neutral reaction to litmus, and is known as "neutral alum," though it is a basic salt. If allowed to evaporate slowly at the ordinary temperature, crystalline crusts are formed which contain the salt, $Al_4(SO_4)_3(OH)_6 + K_2SO_4$. If the solution is heated above $40°$ C., a precipitate of the composition $Al_2(SO_4)(OH)_4 + K_2SO_4$ is formed.

Uses.—Alum is used by many dyers in preference to aluminium sulphate, since the crystalline form assures regular composition. In some cases the ammonium or potassium sulphate introduced into the dye-bath no doubt exerts some influence upon the results obtained. No distinction is made in practice between ammonia and potash alum ; the former contains 37·7 per cent. dry aluminium sulphate, and the latter 36·1 per cent. Alum is used as a mordant in the dyeing of all classes of fibres, though it is not used to such a great extent as it was formerly. In the dyeing of cotton, basic salts are usually employed. Alum is used to some extent in the preparation of aluminium acetate (red liquor) and other aluminium mordants, though for these purposes it has been largely replaced by aluminium sulphate.

Examination and Analysis. — Ammonia alum is readily distinguished from potash alum by evolving ammonia when boiled with caustic soda.

Alum in the crystallised state cannot well be adulterated, but iron and free sulphuric acid may be present as impurities.

Iron may be readily detected by adding a mixture of potassium ferro- and ferricyanides, which quickly produce a blue colour with iron. A greyish-blue colour is *gradually* developed with *pure* alum. Tannic acid may also be used as a test for iron, with which it gives a grey or black coloration. The amount of iron present is best determined colorimetrically (v. WATER).

Free Sulphuric Acid.—For the detection of free acid in alum and aluminium sulphate, Watson Smith * recommends the use of ferric acetate, the red colour of which is destroyed by a trace of free acid. The operation is best performed in a porcelain dish. Congo red, a colouring matter which turns blue with free acids, has been frequently recommended for the same purpose, but it is not a very delicate test.

A preferable method (and one which admits of a ready quantitative determination) is to treat the powdered sample with strong alcohol containing a little phenolphthaleïn and rendered pink with addition of potash. If free sulphuric acid be present the colour is removed, and by titrating the filtered solution with $\frac{N}{10}$ alkali the amount present is readily ascertained.

Alum purchased in the ground state may contain a variety of substances, such as common salt, sodium sulphate, and excess of water. The best method of ascertaining the value of such samples is to determine the *amount of alumina* by precipitation with ammonia. 1 grm. is weighed out and dissolved in about 200 c.c. of water, a considerable amount of ammonium chloride is added, and a *slight* excess of ammonium hydrate. The liquid is kept near the boiling point for some time until the smell of ammonia disappears, when it is filtered and the precipitate well washed with boiling water. The precipitate is dried and ignited in a crucible and weighed as Al_2O_3.

Potash alum contains 10·76 per cent. of alumina (Al_2O_3), and ammonia alum 11·27 per cent.

Chrome Alum v. CHROMIUM.

Aluminium Sulphite, $Al_2(SO_3)_3$. *Aluminium Bisulphite,* $Al(SO_3H)_3$. Sulphurous acid (a strong solution of sulphur dioxide in water) dissolves aluminium hydroxide with formation of one or both of these compounds. Boiling the solutions causes immediate decomposition.

Aluminium Sulphocyanide v. ALUMINIUM THIOCYANATE.

Aluminium Tartrate. — Aluminium hydroxide dissolved in tartaric acid is used to a limited extent for steam colours in calico printing. The pure salt is not known. In mordanting wool with alum and tartar this substance is probably formed in the dye-bath.

Aluminium Thiocyanate or Sulphocyanide, $Al(CNS)_3$.—Aluminium thiocyanate is obtained by the double decomposition of aluminium sulphate with barium or calcium thiocyanate :—

$$Al_2(SO_4)_3 + 3Ba(CNS)_2 = 2Al(CNS)_3 + 3BaSO_4.$$
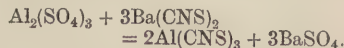
The normal salt can be boiled and even concentrated to a syrupy consistency without being decomposed. The salt, $Al_2(CNS)_5OH$, is also stable ; but the more basic salts are decomposed when boiled ; mere dilution with water will not cause the decomposition of any of these salts.

Aluminium thiocyanate was introduced some years ago by Storck for the production of alizarin reds in calico printing as a substitute for aluminium acetate. It possesses the great advantage that it does not attack the steel doctors of the printing machine, and thus does not introduce iron into the printing colour ; hence the purity and brilliancy of

* *Journ. Soc. Dyers and Col.*, 1884, p. 35.

alizarin red is preserved. The high price of the article has prevented its more general employment, especially in wool dyeing. Very fine results are obtained by mordanting this fibre with aluminium thiocyanate. The wool is introduced into the cold mordanting bath, which is gradually heated to boiling during one and a-half hours. Silk may be mordanted like wool. The thiocyanate is also used in silk printing.

Aluminium Thiosulphate (*Hyposulphite*). —This salt is obtained by double decomposition of aluminium sulphate and calcium thiosulphate. It is known in solution only, and its exact composition has not been determined.

Aluminium thiosulphate was prepared by E. Kopp as early as 1856. He found that the aqueous solution readily decomposes on boiling into aluminium hydroxide, sulphur dioxide, and sulphur; and recommended it to calico printers as a mordant, its advantages being that it was cheaper than aluminium acetate, that it fixed the alumina better on the fibre than the other salts, and that it prevented by its reducing action the oxidation and fixation of iron on the fibre. This mordant, however, has not found general application, since it gives off sulphur dioxide even on drying on the cylinders, and deposits sulphur together with the alumina on the fibres; hence its employment is not advisable. Recently a solution containing alum and sodium thiosulphate has been proposed for mordanting silk previous to dyeing with the alizarins. It is said to have yielded good results on the large scale.

ALUMINATES. — Aluminium hydroxide possesses the character of a weak acid, and forms with basic hydroxides salts which are called aluminates. The aluminates are prepared by melting aluminium oxide with bases or with the corresponding carbonates. Potassium and sodium aluminates are also obtained by dissolving aluminium hydroxide in caustic potash and caustic soda. The aluminates which are produced in the dry way are derivatives of the aluminium hydroxide, $AlO(OH)$—*e.g.*, $(AlOO)_2Ba$. A great many of these occur as minerals. Potassium aluminate is obtained in crystals from aqueous solutions, as

$$Al(OH)_2(OK), \text{ or } 2Al(OH_2)OK + H_2O.$$

Sodium aluminate has not been prepared in the crystalline form. On the whole, the acid character of aluminium hydroxide is less distinct than the basic. The solutions of aluminates are decomposed by all acids, even by carbonic acid; aluminium hydroxide is precipitated and a potassium or sodium salt remains in solution. In a similar way the solutions of aluminates are decomposed by ammonium salts, potash, or soda, as the stronger bases combine with the acid of the ammonium salt, whereas the liberated aluminium hydroxide does not combine with the ammonia, and remains in the free state in the form of a gelatinous precipitate.

$$Al(OH)_2OK + NH_4Cl$$
$$= Al(OH)_3 + KCl + NH_3.$$
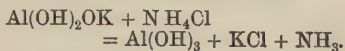
Use is made of this reaction in fixing the mordant.

Aluminate of Soda—*Alkaline Pink Mordant.*—This substance is prepared by melting *cryolite* ($Al_2F_6 . 6NaF$) with lime, or *bauxite* (impure hydrated aluminium silicate) and soda ash. It can also be obtained by adding caustic soda to a strong solution of aluminium sulphate until the precipitate at first formed is re-dissolved, and no fresh precipitate is produced on addition of more caustic lye. A slight excess of alkali makes the solution more stable and is not injurious. If a small amount of caustic lye only is used the precipitate re-dissolves with formation of basic aluminium sulphate; on adding more alkali, however, a fresh precipitate is formed, until all the sulphuric acid is neutralised by the caustic soda. Aluminate of soda occurs in commerce as a lumpy powder of a slightly greenish-white colour. It is readily soluble in water, but not deliquescent, and is decomposed by carbon dioxide in the presence of moisture. It is used as a mordant for alizarin red on cotton piece goods (*Schlieper's process*), but cannot well be employed on cotton yarn on account of the caustic action it has on the hands of the workmen. Aluminate of soda offers the great advantage that it does not carry iron into the ultimate colour, and that it is fixed on the fibre in a short time without ageing. It finds but limited employment, because it cannot be associated with acid mordants. The goods are simply impregnated with the aluminate, rapidly dried at an elevated temperature, and passed through a solution of ammonium chloride (10° Tw.) at 50° to 60° C. The aluminium is thus fixed in the form of aluminium hydroxide. The hydroxide is also fixed to some extent by mere exposure to the atmosphere. Other salts can be substituted for the ammonium chloride — *e.g.*, zinc sulphate, chloride, or acetate. It seems, however, that they do not offer any advantages over the ammonium salts. Aluminate of soda is not used as a mordant for wool or silk, because it is too alkaline for these fibres. For the production of *lakes* the colouring matter is mixed with the solution of sodium aluminate and precipitated by the addition of sulphuric acid. These lakes are considered by Morin to be richer than those obtained from alum, and are produced at about one-half the cost.

Analysis of Aluminate of Soda.—The following method by G. Lunge [*] is applicable

* *Chem. News*, vol. lxiv., p. 187.

when only small quantities of silica are present. A weighed quantity of the sample is dissolved in water and made up to a known volume. The solution is filtered, and after sufficient of the filtrate has been collected the receiving vessel containing it is removed and the insoluble matter collected and washed on the filter, its weight after incineration being noted.

A measured quantity of the undiluted filtrate is next mixed with phenolphthaleïn and titrated whilst hot with normal acid until the red colour disappears. The result shows the quantity of soda combined with alumina or silica. There is then added to the liquid one drop of a solution of methyl orange, and it is titrated further. During the second titration the liquid is to be kept moderately warm, say 30° to 37° C. If necessary, it is either cooled or set in a warm place. The titration is completed when the yellow colour of the liquid changes to a permanent red. As now all the alumina is converted into aluminium chloride or sulphate, the amount of alumina can be calculated from the two titrations. It is at once found in grammes by multiplying the difference of the two readings of the burette by 0·017 if normal acid has been used, or by 0·0017 in case of decinormal acid. In technical determinations small quantities of silica, if present, may be neglected. It is more accurate to determine them and deduct the amount as orthosilicate.

AMARANTH (M.) (C.) (P.). *Fast red I and E B* (B.), *Fast red N S* (By.), *Azo acid rubin 2 B* (D.), *Bordeaux S* (Ber.), *Bordeaux D H* (D. & H.), *Naphthol red O* (M.), *Naphthol red S* (B.), *Victoria rubin* (M.), *Oenanthinin* (D. & H.), *Wool red extra* (K.) An azo compound.

Naphthionic acid — Beta naphthol disulphonic acid R.

1878. Red-brown powder, giving a magenta-red solution in water. In concentrated H_2SO_4, violet solution, becoming crimson on dilution.

Application.—An acid dye. Dyes *wool* and *silk* in an acid bath a pure bluish-red, which is moderately fast to light and milling.

AMETHYST VIOLET (M.) An azine derivative, allied to safranine, *Tetraethyl-safranine chloride.* 1883. Black-grey powder, giving a red-violet solution in water. Soluble in alcohol, with a crimson colour with blue-red fluorescence. In concentrated H_2SO_4, green solution, becoming blue and then blue-violet on dilution.

Application.—A basic dye. Dyes *cotton* mordanted with tannin and tartar emetic a blue-violet. Principally used in *silk* dyeing, giving in neutral bath a violet with red fluorescence.

AMMONIA, NH_3.—Ammonia is a colourless gas, possessing a characteristic pungent smell. It occurs in minute quantities in the air both free and in combination as nitrate and carbonate. This atmospheric ammonia, which can be detected by passing a large amount of air through *Nessler's solution* (an alkaline solution of potassium mercuric iodide which becomes coloured brown), is produced by electric action, by the evaporation of water, and by the decomposition of animal and vegetable matter, &c. The air in towns, although generally giving a slightly acid reaction, contains considerable quantities of ammonia, as is easily demonstrated by testing carefully-collected rain-water with Nessler's reagent.

Ammonia is prepared for laboratory purposes by heating ammonium sulphate with lime—

$$(NH_4)_2SO_4 + CaO = 2NH_3 + CaSO_4 = H_2O.$$
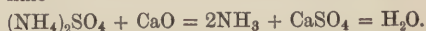
The evolved gas being much lighter than air, having a specific gravity of 0·585 (air = 1), is collected by passing the gas upwards into an inverted cylinder, the air being thus displaced.

Properties.—Ammonia is feebly combustible in air, especially when previously heated, and burns readily in oxygen. It is soluble in alcohol or ether; and certain salts, such as silver chloride, absorb it readily. Faraday liquefied the gas by simply heating the latter compound of ammonia ($2AgCl . 3NH_3$) in one arm of a sealed bent tube, the ammonia passing off and being condensed by its own pressure in the other arm, which was surrounded by ice.

The solubility of ammonia in water is very remarkable, one volume of water at 15° C. dissolving 730 volumes of the gas, which, however, is easily expelled by boiling the liquid. Ammonia can be liquefied by moderate pressure, and the liquid is sold in a comparatively pure state in iron cylinders as *anhydrous ammonia.* When liquefied ammonia is evaporated under reduced pressure, it absorbs heat rapidly from its surroundings, and is on this account largely used in the manufacture of ice in Carré's and Linde's machines. Ammonia, both in the gaseous state and in solution, evinces strong basic properties; it turns red litmus blue, yellow turmeric paper brown, and neutralises acids, forming salts very closely resembling the salts of potassium and sodium. Liquid ammonia dissolves potassium and sodium without change, also sulphur, phosphorus, and iodine. Ammonia is resolved into its constituents by the action of the electric spark or when passed through a red-hot tube, two volumes of ammonia yielding three volumes of hydrogen and one volume of nitrogen.

Ammonium Hydroxide, NH_4OH—*Liquor ammoniæ. Spirits of hartshorn.*—When a solution of ammonium chloride is poured over sodium amalgam, the latter swells

to many times its original bulk. The metalline mass changes its volume like a gas on subjecting it to pressure. This light, buttery substance becomes crystalline at a low temperature, but under ordinary circumstances soon decomposes into ammonia, hydrogen, and mercury. The constituent of this body which corresponds to sodium in the sodium amalgam has not been isolated, but it differs from ammonia by containing one more atom of hydrogen, and consequently is represented by the formula NH_4. This hypothetical compound has been named *ammonium*. From this fact and other considerations the compounds of ammonia with acids are regarded as salts of the monovalent radical ammonium. The analogy will be obvious on examining the following formulæ:—

Potassium chloride, KCl	Sodium chloride, NaCl	Ammonium chloride, NH_4Cl
Potassium hydroxide, KOH	Sodium hydroxide, NaOH	Ammonium hydroxide, NH_4OH

Hence it is assumed that the colourless liquid known as ammonia, and which is a solution of ammonia gas in water, contains the hydroxide, NH_4OH. Considerable heat is evolved when water absorbs ammonia gas, the resulting solution increasing in volume and becoming specifically lighter the more ammonia it contains (see annexed Table).

The strongest solution of ammonia met with in commerce contains about 35 per cent. NH_3, and has a specific gravity of 0·88. This solution dissolves many metallic oxides —*e.g.*, Ag_2O, CuO, ZnO, and also AgCl and Ag_3PO_4. A number of resins are soluble in ammonia, and fats are saponified by it. It acts like caustic potash and soda in precipitating heavy metals from their solutions, as hydroxides.

Manufacture.—Ammonia is prepared on the large scale from gas liquor (which is the aqueous portion of the distillate obtained by the dry distillation of coal in gas works), from coke ovens, and also from blast-furnace gases. Gas liquor is a liquid varying in colour from light yellow to dark brown, of an ammoniacal and empyreumatic odour. Its composition varies considerably, but it usually contains small quantities of tar in suspension, pyridine bases, phenol, and occasionally free ammonia in solution, together with large quantities of ammonium carbonate and sulphide (its chief constituents), and varying amounts of sulphocyanide (thiocyanate), ferrocyanide, chloride, sulphate, thiosulphate (hyposulphite), and sulphite. When ammonium compounds are heated with alkalies or alkaline earths ammonia gas is set free. Gas liquor generally contains 15 to 30 per cent. of ammonia as salts, from which it is set free by distilling with lime. The crude gas thus obtained

SPECIFIC GRAVITY OF LIQUOR AMMONIÆ AT 150° C. (*Lunge and Wiernik*).

Specific Gravity at 15° C.	Per cent. NH_3.	One Litre contains grms. NH_3.*	Correction of the Specific Gravity for ± 1° C.
1·000	0·00	0·0	0·00018
0·998	0·45	4·5	0·00018
0·996	0·91	9·1	0·00019
0·994	1·37	13·6	0·00019
0·992	1·84	18·2	0·00020
0·990	2·31	22·9	0·00020
0·998	2·80	27·7	0·00021
0·986	3·30	32·5	0·00021
0·984	3·80	37·4	0·00022
0·982	4·30	42·2	0·00022
0·980	4·80	47·0	0·00023
0·978	5·30	51·8	0·00023
0·976	5·80	56·6	0·00024
0·974	6·30	61·4	0·00024
0·972	6·80	66·1	0·00025
0·970	7·31	70·9	0·00025
0·968	7·82	75·7	0·00026
0·966	8·33	80·5	0·00026
0·964	8·84	85·2	0·00027
0·952	9·35	89·9	0·00028
0·960	9·91	95·1	0·00029
0·958	10·47	100·3	0·00030
0·956	11·03	105·4	0·00031
0·954	11·60	110·7	0·00032
0·952	12·17	115·9	0·00033
0·950	12·74	121·0	0·00034
0·948	13·31	126·2	0·00035
0·946	13·88	131·3	0·00036
0·944	14·46	136·5	0·00037
0·942	15·04	141·7	0·00038
0·940	15·63	146·9	0·00039
0·938	16·22	152·1	0·00040
0·936	16·82	157·4	0·00041
0·934	17·42	162·7	0·00041
0·932	18·03	168·1	0·00042
0·930	18·64	173·4	0·00042
0·928	19·25	178·6	0·00043
0·926	19·87	184·2	0·00044
0·924	20·49	189·3	0·00045
0·922	21·12	194·7	0·00046
0·920	21·75	200·1	0·00047
0·918	22·39	205·6	0·00048
0·916	23·03	210·9	0·00049
0·914	23·68	216·3	0·00050
0·912	24·33	221·9	0·00051
0·910	24·99	227·4	0·00052
0·908	25·65	232·9	0·00053
0·906	26·31	238·3	0·00054
0·904	26·98	243·9	0·00055
0·902	27·65	249·4	0·00056
0·900	28·33	255·0	0·00057
0·898	29·01	260·5	0·00058
0·896	29·69	266·0	0·00059
0·894	30·37	271·5	0·00060
0·892	31·05	277·0	0·00060
0·890	31·75	282·6	0·00061
0·888	32·50	288·6	0·00062
0·886	33·25	294·6	0·00063
0·884	34·10	301·4	0·00064
0·882	34·95	308·3	0·00065

*The number of pounds of NH_3 per gallon is found by dividing by 100 the number in the third column (grammes of NH_3 per litre).

contains sulphuretted hydrogen, pyridine bases, and other volatile products of coal tar. To eliminate these the ammonia gas is passed through a lime purifier and a small washer containing iron oxide in suspension, next through a coke scrubber, and finally, after being washed in concentrated soda solution, into water in a well cooled saturator. Any ammonia escaping is absorbed by leading into dilute sulphuric acid.

Commercial liquor ammonia should be clear and colourless, the ordinary solution having a specific gravity of 0·91 and containing about 25 per cent. NH_3.

Uses.—Ammonia is employed in many industries (manufacture of ammonia-soda, dyestuffs, &c.) for the purpose of neutralising acids, and in the manufacture of ice by Carré's and Linde's machines. By dyers it is used where a milder alkali than caustic soda is required, or where its volatility allows of the ready removal of the excess of the alkali, as, for instance, in neutralising Turkey-red oil. It is also used as a fixing agent for some metallic mordants—*e.g.*, lead salts and basic iron salts.

Putrid urine and dung are made use of in scouring, and in certain operations in dyeing and printing, owing to the presence of ammonium salts in these substances.

Impurities.—The caustic ammonia prepared from gas liquor frequently contains tarry basic impurities, which gradually undergo decomposition and cause the liquid to assume a yellow or even a brown colour. A second distillation, preferably with the addition of an oxidising agent, is necessary for its purification.

Commercial ammonia should be free from sulphuretted hydrogen and carbonic acid. So-called *sulphate ammonia* is a purified ammonia prepared by distilling ammonium sulphate with lime.

Analysis.—A close approximation of the strength of a solution of ammonia may be ascertained by a careful determination of its density. For this purpose a specific gravity flask marked on the neck to hold 25 grms. of distilled water at 15° C. may be conveniently used. The dry flask is carefully tared, filled with ammonia, and again weighed. The weight of the sample thus obtained divided by 25 gives its specific gravity (water = 1), and on reference to the table the percentage of NH_3 corresponding to the density of the solution is ascertained. The flask should be filled with distilled water at 15° C., and weighed to prove that it really does hold 25 grms. when filled to the mark. The exact weight it contains, if not 25 grms., is then used as the devisor.

The specific gravity may also be taken at the above temperature by means of a delicate hydrometer.

Estimation of Free Ammonia by Titration.—The 25 c.c. of ammonia used in taking the density, of which the weight is known, may be transferred to a 500 c.c. flask, and after carefully washing out the specific gravity bottle, the solution is made up to the mark and thoroughly shaken. Of this solution, 50 c.c. are withdrawn by means of a pipette and titrated in a basin with normal sulphuric acid, methyl orange being used as indicator.

1 c.c. of normal acid = 0·017 of NH_3.

Example.—25 c.c. of a sample of ammonia weighed 22·888 grms. Specific gravity, therefore, $= \dfrac{22·888}{25} = ·9155$. The 25 c.c. were diluted to 500 c.c., and 50 c.c. of this solution required 31·8 c.c. of normal sulphuric acid.

$$\therefore \ \frac{0·017 \times 31·8 \times 10 \times 100}{22·888} = 23·60 \%\ NH_3.$$

The presence of sulphides and tarry matter in gas liquor ammonia is objectionable for some purposes. *Sulphides* may be detected by the violet colour imparted to paper saturated with a solution of sodium nitroprusside. If an empyreumatic odour is gradually developed when a solution of ammonia is allowed to evaporate spontaneously the presence of *tarry matter* is obvious. Commercial samples of ammonia, when neutralised by nitric acid, frequently develop a rose-red colour and a peculiar odour owing to the presence of certain *organic bases.*

Estimation of Combined Ammonia.—The titration of ammoniacal solutions with standard acid as detailed above only shows the amount of free ammonia present. If the ammonia is in combination with an acid, as in ammonium sulphate, the total ammonia may be determined by distilling a weighed amount of the substance in solution with some alkali, preferably caustic soda. The evolved ammonia is collected in a known volume of standard acid and titrated back with standard alkali, or absorbed in an excess of hydrochloric acid and the ammonium chloride thus formed estimated by precipitation with platinum tetrachloride.

The total ammonia found by distillation less the amount found by titration gives the quantity which is present in combination with acids. 1 grm. of the ammonium salt is weighed and transferred to a flask of about 200 c.c. capacity, together with 25 c.c. of water. The flask must have been previously fitted with a rubber cork having two openings, through one of which passes a tapped funnel holding a strong solution (10 per cent.) of caustic soda. A glass tube about 30 inches long is inserted in the other opening and inclined upwards at an angle of about 30° in

order to prevent any alkali being carried over mechanically with the ammonia. The other end of the tube is bent downwards and passed through a cork into a flask of about 500 c.c. capacity containing 40 c.c. of normal sulphuric acid. The outlet of this receiving flask is fitted with a short wide tube containing glass wool or glass beads through which the standard acid has been poured. Both ends of the distilling tube should be cut off at a sharp angle, and the one in the receiver must reach nearly to the surface of the standard acid. During the distillation the receiver must be kept cool by being placed in a vessel of cold water. Heat is applied to the small flask as soon as the caustic soda solution has been run in. The liquid should be boiled for about thirty minutes. The small tube containing the glass wool saturated with sulphuric acid is washed well with distilled water into the flask and the residual acid determined by titration with normal caustic soda, using methyl orange as indicator.

Example.—1 grm. of ammonium sulphate was distilled, as above described, into 40 c.c. of normal sulphuric acid. The acid remaining neutralised 25 c.c. of normal soda; therefore, 15 c.c. of acid were neutralised by the ammonia.

1 c.c. of $\frac{N}{1}$ acid = 0·017 grm. NH_3.

∴ 0·017 × 15 × 100 = 25·50 per cent. NH_3.

If it is desired to estimate the ammonia gravimetrically, hydrochloric acid is placed in the receiver instead of sulphuric acid. After the distillation, the acid solution of ammonium chloride is poured into a porcelain dish, the receiver being of course well rinsed, and after the addition of platinum chloride solution the whole is evaporated *nearly* to dryness on the water-bath. Vapour of ammonia should be carefully excluded or the result will come out too high. The solution should remain highly coloured during the whole of the evaporation. If it become nearly colourless more platinum chloride must be added. When the mass is of a pasty consistency the basin is removed from the water-bath, and when nearly cold 25 c.c. of rectified methylated spirit is poured over it. The crystals should not be broken up, but by gently rotating the dish the alcohol dissolves out the excess of platinum chloride more easily. After standing about ten minutes the supernatant liquid is poured on a small filter which has been previously moistened with hot water and then with alcohol. The precipitate is treated with successive quantities of alcohol until the filtrate comes through colourless, and leaves no more than the slightest stain when a drop or two are evaporated on a watch-glass. The bulk of

the platinum double salt remaining in the basin is transferred to a small weighed platinum or porcelain basin, and the small amount on the filter is washed into the basin with hot water. The liquid is evaporated to dryness, and dried at 100° C. in the water-oven until of constant weight. 442·5 parts of the precipitate correspond to 34·02 parts NH_3.

Example.—0·5 grm. ammonium sulphate was distilled with soda, as explained above, and the acid distillate on treating with platinum chloride yielded 1·6785 grm. $PtCl_4 . 2(NH_4)Cl$.

$$\frac{1·6785 \times 34·02 \times 100}{442·5 \times ·5} = 25·81°/_o NH_3.$$

Carbonic acid is easily recognised on adding calcium chloride solution to the ammonia. The resulting precipitate of calcium carbonate may be filtered off, washed, and dissolved in normal acid. The excess is titrated back with alkali.

1 c.c. $\frac{N}{1}$ acid = 0·022 grm. CO_2.

The analysis of liquid ammonia as used in freezing machines is generally restricted to the determination of the non-volatile residue, which consists chiefly of an oil containing pyridine, acetonitril, alcohols, and mineral matter. A. Lange and J. Herz * take 20 to 50 grms. in a tared Erlenmeyer flask fitted with a stopper having two perforations for a potash tube and a bent glass tube; the latter being closed and the former open, all the ammonia must pass through the potash tube. After about three hours at the ordinary temperature most of the ammonia will have escaped. The temperature is raised to 40° C. and dry air free from carbon dioxide passed through, and the whole apparatus after closing the tubes is weighed on cooling. Unfortunately small quantities of the organic residue are carried away mechanically by the escaping ammonia. H. von Strombeck † considers that the explosions which occur occasionally in refrigerating plant are due to these organic impurities and proposes to destroy them by passing the dry ammonia gas through sodium kept in a liquid state.

In the ordinary commercial liquid ammonia the non-volatile residue, including the moisture which is retained by the potash, is about 1·3 per cent.

Ammonium Acetate, $CH_3 . COONH_4$.— This salt is prepared by saturating glacial acetic acid with ammonia gas. The crystals obtained by this process have an odour of acetic acid. They are exceedingly soluble in water and alcohol, but do not deliquesce in the air. A solution of ammonium acetate may be made by neutralising acetic acid with ammonia. On evaporation of the mixture

* *Journ. Soc. Chem. Ind.*, 1897, p. 467.
† *Ibid.*, 1892, p. 736.

ammonia is expelled, and the acid acetate or diacetate is produced.

Ammonium acetate has been recommended as an addition to the dye-bath in the dyeing of woollen goods with alizarin.

The crystals, if pure, are completely volatilised on heating.

Ammonium Carbonate, $(NH_4)_2CO_3 . H_2O$.— The normal salt is a very unstable body. It separates out as a crystalline powder when ammonia gas is passed through a concentrated solution of commercial ammonium carbonate. On exposure to air the crystals lose ammonia and become opaque, forming acid ammonium carbonate. On merely dissolving the salt in water the same reaction takes place, and the acid carbonate results.

Ammonium Carbamate, $CO \begin{cases} N H_2 \\ O N H_4 \end{cases}$.— When dry carbonic acid gas and ammonia gas are brought together this substance is deposited as a white saline mass—

$$CO_2 + 2NH_3 = CO \begin{cases} NH_2 \\ ONH_4 \end{cases}$$
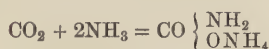
It is the ammonium salt of carbamic acid, $CO \begin{cases} NH_2 \\ OH \end{cases}$. It smells strongly of ammonia, and volatilises at 60°C. On dissolving in water it is converted into normal ammonium carbonate—

$$CO \begin{cases} NH_2 \\ ONH_4 \end{cases} + H_2O = CO \begin{cases} O \cdot NH_4 \\ O \cdot NH_4 \end{cases}$$
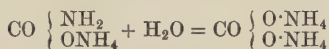
Ammonium Sesquicarbonate, $(NH_4)HCO_3 + CO \begin{cases} NH_2 \\ ONH_4 \end{cases}$ – Sal volatile, Salt of hartshorn, Commercial carbonate of ammonia. This salt is formed by the putrefaction of nitrogenous substances like urine. In former times it was obtained by the dry distillation of hide clippings, bones, or horn, hence the name salt of hartshorn (and spirit of hartshorn for ammonia water). At the present time commercial ammonium carbonate is manufactured on the large scale by heating a mixture of ammonium sulphate and chalk in cylindrical cast-iron retorts. The vapours are led into cooling chambers and condensed. The crystals are deposited as a white semi-transparent fibrous mass, and the vapours of uncondensed ammonium carbonate and ammonia (which is always present) are condensed in sulphuric acid. The crude ammonium salt when removed from the cooling chambers still contains tarry matters, from which it is purified by sublimation in iron pots placed in hot water. The sublimate smells of ammonia and is very soluble in water. It is really a sesquicarbonate of ammonia and may be considered a mixture of equal molecules of ammonium bicarbonate and ammonium carbamate,

$$CO \begin{cases} OH \\ ONH_4 \end{cases} + CO \begin{cases} NH_2 \\ ONH_4 \end{cases}$$
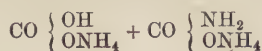
When the salt is dissolved in water the ammonium carbamate is decomposed (v. AMMONIUM CARBAMATE), the normal carbonate and eventually the bicarbonate of ammonia being produced. The crystals of commercial ammonium carbonate smell of ammonia, and absorb moisture and carbon dioxide from the air, the ammonium carbamate being thus converted into bicarbonate of ammonia. If sal volatile be dissolved in concentrated ammonia solution, crystalline plates of normal ammonium carbonate separate out. On treating with alcohol, the latter salt is dissolved, while the acid carbonate of ammonia remains undissolved. Commercial ammonium carbonate is used for scouring wool and for fixing aluminium mordants on cotton. It should dissolve in water, forming a colourless solution, and when heated on platinum foil should volatilise without leaving any residue. The ammonia may be determined by the distillation method with caustic soda or by adding an excess of normal sulphuric acid and titrating back with normal alkali, using methyl orange as indicator.

Ammonium Bicarbonate ; Acid Ammonium Carbonate, $NH_4 HCO_3$. — Ammonium bicarbonate is usually prepared by passing carbonic acid gas through a saturated aqueous solution of the sesquicarbonate. The ammonium carbamate, on dissolving in water, forms this normal ammonium carbonate which is then decomposed, as shown by the equation—

$$CO \begin{cases} O \cdot NH_4 \\ O \cdot NH_4 \end{cases} + CO_2 + H_2O = 2CO \begin{cases} OH \\ O \cdot NH_4 \end{cases}$$
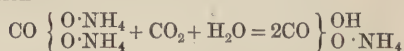
The salt forms small crystalline plates, which dissolve in 7 or 8 parts of water. It contains 21 to 23 per cent. of NH_3, whereas commercial ammonium carbonate — i.e., the sesquicarbonate—contains 31 per cent. NH_3.

Ammonium bicarbonate does not smell strongly of ammonia, and on exposure soon loses all odour. It has been found in guano, and is occasionally met with in brilliant rhombic crystals in the purifiers of gas works.

Ammonium Chloride, NH_4Cl. Sal Ammoniac. Muriate of Ammonia.—This is made by absorbing the ammonia evolved during the distillation of gas liquor, in hydrochloric acid. Lead vessels should be avoided, as lead is attacked by hot hydrochloric acid. The ammonium chloride solution is evaporated in wooden tanks, through which passes an iron steam coil. When iron evaporators are used it is necessary to keep the solution just alkaline by the continual addition of small quantities of ammonia, as a boiling solution of ammonium chloride decomposes slightly and becomes acid. The crude ammonium chloride is drained and dried on plates, and then freed from tarry matters and other

impurities by sublimation from iron pots. This product is the commercial *sal ammoniac*.

Ammonium chloride is also prepared by adding a slight excess of hydrochloric acid directly to gas liquor. The solution, after separation from sulphur, is evaporated to crystallisation. The crystals have an unpleasant smell, and are red or yellow in colour. By dissolving this raw material in water, passing the solution through a layer of animal charcoal, and subsequently crystallising, the so-called *muriate of ammonia* is obtained.

In the manufacture of sodium carbonate by the ammonia process, ammonium chloride is produced as a by-product. When concentrated solutions of ammonium sulphate and sodium chloride in equivalent proportions are mixed and evaporated, sodium sulphate separates out, and ammonium chloride remains in solution.

Ammonium chloride, on volatilising, decomposes into NH_3 and HCl, which recombine, on cooling, to form the original substance.

Uses.—Ammonium chloride is used in soldering, in galvanising iron, for fixing aluminate of soda on the cotton fibre, and in dyeing aniline black.

Analysis.—The chemical examination generally consists of an estimation of the ammonia by the distillation process, and the determination of the chlorine by titration with $\frac{N}{10}$ $AgNO_3$, using potassium chromate as indicator.

Empyreumatic substances are detected by their action in decolourising a dilute solution of potassium permanganate.

Iron, which is detrimental to the employment of the salt in dyeing, may be estimated by colour titration with potassium ferrocyanide, or, if much be present, by first reducing with a little zinc and hydrochloric acid, in order to convert all the iron into the ferrous condition, and then titrating with standard potassium permanganate.

Ammonium Chromate, $(NH_4)_2CrO_4$, is obtained in the form of long yellow needles by saturating a solution of chromic acid (CrO_3) with ammonia. On igniting the crystals, oxygen and ammonia are evolved and chromium sesquioxide (Cr_2O_3) remains. Ammonium chromate is employed in calico printing.

Ammonium Bichromate, $(NH_4)_2Cr_2O_7$, crystallises in large red crystals. It is prepared by adding the requisite quantity of chromium trioxide (CrO_3) to the normal salt. According to J. Park's patent, calcium chromate is treated with the necessary amount of sulphuric acid to convert it into calcium bichromate, and to this a solution of ammonium sulphate is added. The whole is

filtered from calcium sulphate and evaporated to the crystallisation point.

Ammonium Oxalate $\left\{ \begin{array}{l} COONH_4 \\ COONH_4 \end{array} \right. \cdot H_2O.$—This salt is prepared by saturating a solution of crude oxalic acid with crude caustic ammonia, the solution is purified by filtration or subsidence, and the clear liquid evaporated to the crystallising point. The crystals of neutral ammonium oxalate may be dissolved in water, passed through animal charcoal and re-crystallised, if a pure product is required. Ammonium oxalate is used in calico printing.

The acid salt $\left\{ \begin{array}{l} COOH \\ COONH_4 \end{array} \right.$ is formed by using half the quantity of ammonia which had been calculated as necessary to produce the neutral salt.

Ammonium Sulphate, $(NH_4)_2SO_4$.—Ammonium sulphate is produced in large quantities by treating gas liquor with lime in continuous stills and absorbing the free ammonia in dilute sulphuric acid. The solution is evaporated and the crystals fished out, drained, and dried.

Uses.—Ammonium sulphate is used in the ammonia soda process, and in the preparation of caustic ammonia and other ammonium salts, besides being employed as a manure.

Analysis.—The commercial salt is generally moist, and the *water* should be determined by drying a weighed quantity in a watch-glass at 110° C. until it ceases to lose weight. The crystals often contain a little *free acid*, which may be estimated by dissolving a weighed amount in water and titrating with $\frac{N}{5}$ soda.

$$1 \text{ c.c. } \tfrac{N}{5} \text{ NaOH} = 0.098 \text{ grm. } H_2SO_4.$$

The *total amount of sulphuric acid* is determined by dissolving 0.5 grm. of the crystals in water in a beaker, acidifying with hydrochloric acid and heating to the boiling point. An excess of a hot solution of barium chloride solution is added and the precipitate left a few hours to settle. A drop of barium chloride is added to prove that all the sulphate has been precipitated, the supernatant liquid is decanted and poured on a previously well-fitted and wetted filter. The precipitate having been well washed with hot water by decantation, is brought on the filter and washed until the filtrate ceases to give an opalescence with silver nitrate solution. After drying, the precipitate is detached from the filter paper and transferred to a weighed porcelain crucible, the filter paper being separately folded into small compass, wrapped in platinum wire, and ignited, the ash being added to the crucible. The crucible and its contents are ignited, with free access of air, and weighed when cold.

The weight of barium sulphate found (after

subtracting the filter ash) is converted into percentage of H_2SO_4 as follows :—

$$\frac{\text{wt. } BaSO_4 \text{ found} \times 100 \times 98}{\text{wt. of salt taken} \times 233} = \text{per ct. } H_2SO_4.$$

When the percentage of H_2SO_4 previously found in titration is subtracted from the total amount found by precipitation, the quantity of combined H_2SO_4 is ascertained. The latter figure $\times \frac{96}{98} =$ percentage of combined SO_4.

The *ammonia* is determined by the distillation method. Ammonium sulphate is completely decomposed and volatilised by ignition on platinum foil.

The commercial substance sometimes contains ammonium thiocyanate, which is considered injurious to vegetation, hence if required for use as a manure the absence of this body should be demonstrated. A rough test for its presence is to pour a few drops of ferric chloride on to a small heap of the salt on a watch-glass, when a red coloration of ferric thiocyanate will be produced. The amount may be approximately estimated by adding a solution of ferric chloride to about 3 grms. of pure ammonium sulphate crystals on which has been dropped a definite amount of ammonium thiocyanate solution from a burette, and comparing the colour developed by a like weight of the crystals to be tested with the same amount of ferric chloride.

Ammonium Sulphocyanide or Thiocyanate, NH_4CNS.—The manufacture of this substance has lately assumed some importance. It occurs in gas liquor to the extent of 2 to 3 parts per 1000, and also in the *spent oxide* which has been used in the purification of coal gas. When an alcoholic solution of ammonia is mixed with carbon bisulphide and allowed to stand for some days, and then the alcohol expelled by evaporating the mixture to about one-third of its original bulk, colourless crystals of ammonium thiocyanate separate out.

$$CS_2 + 4NH_3 = NH_4CNS + (NH_4)_2S.$$

On the large scale the salt is made by systematically lixiviating spent oxide until a solution containing about 2 per cent. of ammonium sulphocyanide is obtained. If sufficiently pure, the liquid is evaporated and, after separating the crystals of ammonium sulphate, the mother liquor is concentrated until ammonium sulphocyanide crystallises out.

A better method is the precipitation of the substance from the 2 per cent. solution as copper sulphocyanide, $Cu(CNS)_2$, a fine white powder formed by the addition of a solution of copper sulphate containing sulphurous acid. By treating the precipitate with ammonium sulphide, copper sulphide is thrown

down, and on filtering and evaporating the solution crystals of ammonium sulphocyanide are deposited. The salt is very easily soluble in water and in alcohol, from which it crystallises in large deliquescent laminæ. It is slightly volatile in steam, hence its presence in the salts of ammonia prepared by distilling gas liquor.

The salt melts at 159° C., and on further heating to about 170° is transformed into the isomeric substance *thiourea* $CS \begin{cases} NH_2 \\ NH_2 \end{cases}$.

Ammonium sulphocyanide, as well as other sulphocyanides, is employed in dyeing and calico printing.

Ammonium Vanadate, NH_4VO_3.—Vanadic acid occurs in combination with lead and copper in several rare minerals, such as *mottramite.* It is extracted by means of hydrochloric acid, and the salt evaporated with ammonium chloride when ammonium metavanadate, NH_4VO_3, separates. This salt is impure and, after re-crystallisation, is ignited, the residue, V_2O_5, dissolved in ammonia, filtered, and crystallised.

The salt forms a white crystalline powder, which is sparingly soluble in water and insoluble in alcohol. A solution of an alkaline vanadate on agitation with hydrogen peroxide and ether causes the aqueous solution to become violet in colour. On mixing neutral ammonium vanadate with tincture of galls a deep black colour is produced which does not, however, appear to be permanent.

Ammonium metavanadate finds application in calico printing and cotton dyeing for the production of black. One part of the salt is sufficient to convert 270,000 parts of aniline salt into aniline black, if a sufficient quantity of potassium chlorate be also present.

Toerensen[*] recommends the use of a solution of 1 lb. of ammonium metavanadate in 10 gallons of water for producing a permanent black on leather which has been tanned with nut galls.

AMYL ALCOHOL or ISOBUTYL CARBINOL, $C_5H_{11}(OH)$, is the chief constituent of the *fusel oil*, obtained in the rectification of potato spirit. It is a colourless liquid possessing a peculiar penetrating smell; it dissolves in alcohol and ether, but is not miscible with water, one part only dissolving in 50 parts of water. The specific gravity is 0·8104 at 20° C., and the boiling point 132° C. It yields on oxidation *valeric acid.* In its chemical properties amyl alcohol resembles ethyl alcohol.

AMYLOID *v.* COTTON.

ANALYSIS AND VALUATION OF COAL-TAR COLOURS *v.* COAL-TAR COLOURS.

ANCHUSIN *v.* ALKANET.

ANIL *v.* ANILINE.

ANILEINE, an old name for *Rosolan* or *Mauveine.*

[*] *Journ. Soc. Chem. Ind.*, vol. i., p. 185.

ANILINE, $C_6H_5NH_2$. Aniline was discovered in the products obtained from the dry distillation of indigo by Unverdorben in 1826. Knecht has recently shown that Hellot had probably already discovered aniline previous to 1750. It was termed *crystallin* by Unferdorben. About 1834 it was detected in coal tar by Runge, who called it *kyanol*. Zinin in 1840 prepared it by reducing nitrobenzol with ammonium sulphide. He gave the product the name *benzidam*. The distillation of indigo with caustic potash was carried out by Fritsche in the same year. Among the compounds produced was aniline, the name being derived from the Spanish word *añil* meaning indigo. A. W. Hofmann established the identity of the above substances shortly afterwards. After the discovery of *mauve* by Perkin in 1856 aniline acquired considerable commercial importance.

Preparation.—For the production of aniline, benzene is converted into nitrobenzene by treatment with nitric and sulphuric acids :—

$$C_6H_6 + HNO_3 = C_6H_5 . NO_2 + H_2O.$$

The product is then reduced with hydrochloric acid and iron.

$$C_6H_5NO_2 + 3H_2 = C_6H_5NH_2 + 2H_2O.$$
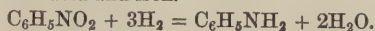
When the reaction is at an end the aniline is driven over by means of steam.

Properties.—Aniline is a colourless liquid having a peculiar smell. It soon becomes brown under the influence of light and air. It solidifies in a freezing mixture and melts again at $-8°C$. When taken internally the oil, which has a burning taste, is poisonous. The vapour, when inhaled, acts similarly, causing a dangerous illness (*anilisme*), which is not uncommon in aniline works. Aniline has no action on litmus. One part of aniline is soluble in 31 parts of water at $12.5°$; it dissolves in all proportions in a 50 per cent. solution of aniline hydrochloride in water. Aniline is easily soluble in alcohol and ether, and itself dissolves sulphur, phosphorus, indigo, aniline blue, and camphor. It burns with a smoky flame on ignition.

Ammonia expels aniline from its salts in the cold, but on heating ammonium salts with aniline, ammonia is set free. Aniline is readily affected by chemical agents, its oxidation under different conditions being of great importance in the production of dyestuffs and in dyeing. A solution of bleaching powder causes a solution of aniline to assume a violet colour. A pine splinter turns yellow when moistened with an aniline salt. On adding a drop of aniline to sulphuric acid and a little potassium bichromate, a red coloration is produced, which eventually becomes deep blue.

Aniline dissolves about 5 per cent. of water, which may be mostly expelled by distillation, as it comes over with the first portion of the distillate. Solid caustic potash removes the last traces of water when agitated and allowed to remain some time in contact with it. The specific gravity of pure aniline at $15°C$. is 1.0268, that of orthotoluidine (methylaniline) is 1.0000. The so-called "aniline for black" is almost pure aniline. The "aniline for red" is obtained similarly to pure aniline, from a mixture of 25 per cent. benzene and 75 per cent. toluene. After nitrating and reducing, a crude "aniline for red" containing about 25 per cent. aniline and 75 per cent. toluidine is produced. The specific gravity of "aniline for red" is adjusted by adding one or other of the amido compounds mentioned to obtain a mixture which will give the required shade of red.

Impurities.—Commercial "pure aniline oil" contains traces of insoluble hydrocarbons, orthotoluidine, and sometimes traces of sulphuretted hydrogen, nitrobenzene, benzene, ammonia, and amidothiophene. A good sample should not contain more than $\frac{1}{2}$ per cent. of water.

Analysis.—The specific gravity is ascertained by means of the specific gravity bottle. To find the boiling point of a sample, R. J. Friswell [*] proceeds as follows :—250 c.c. of the aniline oil are distilled in a flask with side tube through a condenser into a 250 c.c. graduated cylinder. A few pieces of platinum wire or fire-brick previously dropped into the flask cause the liquid to boil more regularly. The flask should be held by a clamp above the side tube, *directly* over a small flame. A good thermometer should be suspended by means of a cork in the neck of the flask, the top of the bulb being placed just below the side tube. It is usual to take the temperature at which the first drop of distillate falls off the end of the side tube.

The temperature of the ascending vapour is carefully observed and recorded at the completion of every 25 c.c. (*i.e.*, 10 per cent. of the whole), any fluctuation being specially noted. The temperature indicated by the thermometer when the flask becomes *just* dry is also of importance.

Insoluble oils may be detected by dissolving 10 c.c. in an equal volume of hydrochloric acid and diluting with water to 100 c.c. The best samples show only a slight opalescence when thus treated, and the smell of the insoluble oils, nitrobenzene, naphthalene, &c., is always distinguishable. Friswell also states that on violently shaking the sample of aniline for a few minutes the smallest trace of nitrobenzol may be distinguished by the froth assuming a distinct yellow colour.

According to Liebermann and Studer [†] the

* *Thorpe's Dictionary of Applied Chemistry.*
† *Journ. Soc. Dyers and Col.*, 1899, p. 107.

estimation of *water* is carried out at the same time as the boiling point is determined. They distil 100 c.c. aniline and collect the first 10 c.c. of the distillate. To this is added 1 c.c. of saturated salt solution, the mixture is well shaken, allowed to settle, and the volume of salt solution read off. Aniline oil, containing 0·3 per cent. water, causes no increase in volume of the salt solution, consequently 0·3 c.c. must always be added to the amount of salt solution observed. The specific gravity at 15° C. is taken on the remaining part of the distillate after removal of the water. This varies in good oils from 1·0265 to 1·027. At least 80 per cent. of the oil should boil within ½° C. of 183° C.

Sulphur compounds, if present, are evolved as sulphuretted hydrogen when the sample is boiled. If during the distillation a paper moistened with lead acetate exposed to the vapour (not immersed in the oil) be coloured light brown, traces of sulphur are present. Should the paper be blackened, the quantity of *sulphur* is determined by boiling a weighed amount of the oil, using a reversed condenser and passing a current of carbon dioxide through the apparatus, the gas being bubbled through a known volume of $\frac{N}{10}$ silver nitrate. The silver sulphide is filtered off and the filtrate titrated with hydrochloric acid. The difference is calculated to silver sulphide and eventually sulphur.

Determination of Aniline in Presence of Small Quantities of Toluidine and vice versâ. —The authors have adopted a method used by Reinhardt [*] for the estimation of aniline, o- and p-toluidine in commercial aniline oil. The method is founded on the following reactions :—

When a solution of aniline in dilute acid is treated with a mixture of potassium bromide and bromate it is converted into tribromaniline, whilst o- and p-toluidine under similar treatment yield dibromo derivatives. The brominating solution is prepared from 480 grms. of bromine, 336 grms. potassium hydrate (100 p. c.), and 1 litre of water ; the solution is boiled for two to three hours and then diluted to 9 litres.

In conducting an analysis 1·5 to 2 grms. of the oil are dissolved in a mixture of potassium bromide and hydrochloric acid equivalent to 100 c.c. of hydrobromic acid (sp. gr. 1·46) and 1000 c.c. of distilled water, and the brominating solution is added until a reaction is obtained with potassium iodide and starch paper.

The brominating solution being standardised against pure aniline, the toluidine value is obtained by multiplying the aniline value by $\frac{160·5}{93}$.

* P. Dobriner and W. Shranz, *Journ. Soc. Chem. Ind.*, 1896, p. 298 ; *Journ. Soc. Chem. Ind.*, 1893, p. 954.

When an oil contains only aniline and the two toluidines, and is free from water, one titration gives the amount of the constituents according to the following equation :—

$$x = 2·3777 \ vt - 1·3777 \ a,$$

in which a = weight of oil taken, x the amount of aniline, t = value of the brominating solution calculated on pure aniline, and v = the number of c.c. of brominating solution taken. Then $a - x$ = amount of toluidine contained in the oil.

In the case of toluidine containing small quantities of aniline, titrate the bromine solution against pure toluidine and calculate the aniline value t by multiplying it by $\frac{93}{160·5}$. It is indeed preferable to designate the value of the brominating solution in c.c. against pure aniline as t, and against pure toluidine as T, then the amount of aniline is given by the equation—

$$\frac{x}{t} + \frac{x - a}{T} = v.$$

The method can also be employed for the valuation of aniline hydrochloride, which for the purpose of analysis must be dried over sulphuric acid. The formula becomes

$$X = 2·5102 \ VT - 1·5102 \ A, - A.$$

X and V have here also corresponding values to those given above. T is the value of the brominating solution in pure aniline hydrochloride, and is obtained from the aniline value t by multiplying by $\frac{129·5}{93}$.

The end of the reaction is detected by spotting on starch-iodide paper. With p-toluidine it is advisable to run in the brominating solution slowly at the beginning and towards the end of the reaction. About 150 c.c. of the brominating solution (1 litre = 8 grms. of aniline) are taken for a determination, the readings being observed very carefully at 15° C.

Aniline Hydrochloride, $C_6H_5NH_2 . HCl.$— *Aniline Salt.* This is prepared by mixing 100 parts of pure aniline with 133 parts of strong hydrochloric acid in stoneware vessels. The salt which crystallises out is drained in a centrifugal machine and dried. The acid used should contain mere traces of iron, and be absolutely free from copper, or the resulting salt will become black.

After removing the crystals the aniline remaining in the mother liquor may be recovered by neutralising with lime or soda.

Aniline hydrochloride forms large colourless crystals, easily soluble in water and alcohol. The salt sublimes at 192° C.

It is used in large quantities in the dyeing and printing of aniline black.

With platinum tetrachloride it forms a double salt $2(C_6H_5NH_2 . HCl) . Pt.Cl_4$.

Impurities—Aniline salt should be free from sand and grit, otherwise tho printing machines may suffer injury.

In order to ascertain the purity or otherwise of the aniline from which the salts were manufactured it is necessary to obtain a little of the oil in the free state. For this purpose a little of the "salts" is decomposed by the addition of caustic soda to the aqueous solution, and extracting the liberated aniline with ether. After evaporating the solvent from the ethereal extract, a few c.c. of the residual aniline are then heated for some time at 180° C. with an equal bulk of arsenic acid solution and the resulting mixture extracted with boiling water. If toluidine were present originally, the aqueous solution is coloured more or less crimson, according to its amount. No coloration is produced if the aniline be pure.

A practical test can also be made by making up a small quantity of colour with the sample salts and pure salts, printing off side by side on a fent, steaming, &c., and comparing the results obtained in depth and purity of shade.

Aniline Sulphate, $(C_6H_5 NH_2)_2 H_2SO_4$.— This body is prepared in a similar manner to the hydrochloride. It is sparingly soluble in water and in alcohol. In ether it is insoluble. An unstable acid sulphate, $C_6H_5NH_2 . H . H_2SO_4$, has been prepared.

ANILINE BLACK. An insoluble black pigment produced by the oxidation of aniline. Discovered in 1834 by Runge ; composition unknown. Three products of the oxidation of pure aniline are distinguished : — (1) *Emeraldine or azurine.* The former is a green coloured salt, the latter a blue coloured base. It is insoluble in water but soluble in alcohol. In concentrated H_2SO_4 it dissolves with a violet-red colour. (2) *Nigraniline* formed by further oxidation of *emeraldine.* Its empirical formula is C_6H_5N, the molecular formula being some multiple of this. The base has a violet-black colour, but its salts are greenish-black. It is insoluble in alcohol but slightly soluble in aniline or phenol. In concentrated H_2SO_4 it gives a violet solution, being converted into sulphonic acids, the alkaline salts of which are soluble in water. By vigorous oxidation nigraniline is converted into *quinone* $(C_6H_4O_2)$, and by powerful reduction it forms *paraphenylene diamine*, $C_6H_4(NH_2)_2$, and *diamido diphenylamine*, $NH(C_6H_4 . NH_2)_2$. Moderate oxidation converts it into *ungreenable black*, and moderate reduction into *emeraldine*, these actions having an important practical bearing. On boiling with aniline it is converted into an insoluble *induline.* (3) *Ungreenable black*, formed by the oxidation of *nigraniline*, is a black substance which con-

tains oxygen in combination. It does not form salts with acids but combines with metallic oxides. By mild reducing agents it is not converted into *nigraniline* but into a leuco (colourless) compound, from which the black is regenerated on exposure to air.

Pure aniline gives the finest black by oxidation, but it is also most prone to the defect of "greening." *Orthotoluidine* produces a violet-black which does not readily become green. *Paratoluidine* produces a dark yellow-brown, *xylidine* (coml.) a dark olive-brown. *Paraphenylenediamine* gives a brownish-black, but a mixture of 1 molecule of this base with 2 or 3 molecules aniline produces a good ungreenable black (Monnet's aniline black). Other aromatic bases yield similar products on oxidation—*e.g., alpha-naphthylamine* gives a brownish-violet (*v.* NAPHTHYLAMINE VIOLET).

Application.—*Aniline black powder*, being insoluble in all common reagents, can only be applied by printing processes. It is employed to a limited extent in calico printing. When used in dyeing processes, aniline black must be produced upon the fibre by oxidation. *Wool dyeing.*—Aniline black is rarely used on wool on account of the difficulty of satisfactorily producing it on this fibre. This is due largely to the powerful reducing action exerted by wool fibre, which must be counteracted by previous or simultaneous oxidation of the fibre. As oxidants for the fibre the following have been proposed —*bleaching powder, potassium permanganate*, and *potassium ferricyanide.* The dyeing takes place hot with ingredients similar to those used for cotton. *Cotton dyeing.* — Aniline black is of great importance in cotton dyeing, a large number of patents covering various details and methods of application having been taken out since it was first successfully applied in 1863. The essential ingredients in an aniline black dye-bath are aniline oil, a mineral acid, and an oxidising agent ; but usually some metallic salt is also added, certain metals — *e.g.*, vanadium, cerium, copper, manganese, and iron—having a most remarkable effect in inducing the oxidation of aniline. The action of vanadium salts is particularly remarkable, 1 part of this metal being sufficient to transform 270,000 parts of aniline into black. The black is not produced in the absence of free acid, but a mere trace is sufficient to induce its formation. As oxidising agents, chlorates and chromates are the most usual, the metallic oxides serving as oxygen carriers. With a given proportion of ingredients the formation of the black is accelerated by raising the temperature or by increasing the concentration of the bath. Practically, however, the black must be developed slowly, since there is otherwise great loss through precipitation of the black in the dye-bath, and superficial fixation causes

the dyed fibre to "rub off" badly. Both cold and warm processes are used, but when dyed in a warm solution the bath is used more dilute and the amount of oxidising agent reduced. Another method frequently employed is to dye in a cold solution and subsequently steam, the utility of the steaming being based upon the fact that a black produced at an elevated temperature does not green so readily as one dyed entirely in the cold. A fourth process is to pad in a cold concentrated solution and then develop by ageing or steaming. In many processes the black undergoes a supplementary oxidation after the actual dyeing operation; the object of this, which usually consists in a treatment with chromic acid solution, is to convert the readily greenable *nigraniline* into *ungreenable black*. After the completion of the process the blacks are always soaped, and sometimes oiled. When properly dyed, aniline black is an extremely permanent colour, being practically unaffected by the light or by acids, alkalies, milling, &c., &c. It is, however, subject to certain *defects*, viz.:—(1) The fibre is frequently (but by no means necessarily) injuriously affected in strength either by the use of too strongly acid solutions or by the production of oxycellulose; (2) the colour is apt to "rub off" on account of superficial fixation; (3) many aniline blacks become green on treatment with acids (particularly sulphurous acid) for reasons already specified. When prepared by means of a chromate, aniline black always contains chromic oxide, and may therefore be topped with mordant dyes, which process reduces the liability to rub. Another process, which also serves to produce very fast blacks, is to dye a medium shade with aniline black and then top with a direct cotton colour, which may be fixed either by a subsequent chroming (*e.g.*, benzo-chrome black) or by diazotising and developing (*e.g.*, diamine black R O).

ANILINE BLUE *v.* SPIRIT BLUE.

ANILINE BROWN *v.* BISMARCK BROWN.

ANILINE GREEN *v.* ALDEHYDE GREEN.

ANILINE ORANGE. *Victoria orange, Victoria yellow, English yellow, Safron substitute.* A nitro compound. *Mixture of potassium (or ammonium) salts of dinitro-orthocresol and dinitro paracresol.* 1869. Reddish-yellow powder, soluble in water. In concentrated H_2SO_4, light yellow solution. On heating the powder the potassium salt deflagrates; the ammonium salt burns quietly.

Application.—An acid dye. Dyes *wool* and *silk* orange in an acid bath. Little used in dyeing. Employed for colouring butter, liqueurs, &c.

ANILINE PINK. Old name for *safranine.*

ANILINE PURPLE. Old name for *rosolan.*

ANILINE RED *v.* MAGENTA.

ANILINE ROSE. Old name for *safranine.*

ANILINE SPIRITS *v.* TIN SPIRITS.

ANILINE VIOLET. Old name for *rosolan.*

ANILINE YELLOW (D. & H.). *Spirit yellow G* (K.) (C.R.). An azo compound. *Amido azobenzene hydrochloride.* 1861. Steel blue crystals, slightly soluble in water with a yellow colour, the solution being gradually decomposed on boiling. In concentrated H_2SO_4, brown solution, becoming red on dilution.

Application.—Not used in dyeing. Used in the preparation of acid yellow and induline. Employed also in colouring lakes, &c.

o-ANISIDINE, $C_6H_4{<}^{NH_2}_{O.CH_3}$.—Ortho-anisidine is a colourless liquid boiling at 226·5° C. obtained by the reduction of ortho-nitranisol, $C_6H_4{<}^{NO_2}_{O.CH_3}$, with iron and hydrochloric acid.

ANISIDINE SCARLET. *Anisol red.* An azo compound.

Orthoanisidine — Beta-naphtholmono-sulphonic acid S

1878. Brownish-red powder. Cherry-red solution in water. In concentrated H_2SO_4, magenta-red solution; cherry-red on dilution.

Application.—An acid dye. Now little used. Dyes *wool* and *silk* bright red from an acid bath.

ANISOL RED *v.* ANISIDINE SCARLET.

ANISOLINE (Mo.). *Rhodamine 3 B* (B.) (S.C.I.). A phthaleïn derivative. *Ethyl ether of tetra ethylrhodamine hydrochloride.* 1892. Brown-red powder, giving violet-red solution in water. Soluble in alcohol, with fluorescence. In concentrated H_2SO_4, green-ish-yellow solution, becoming red on dilution.

Application.—A basic colour. Dyes *wool*, *silk*, or tannin mordanted *cotton* a brilliant bluish-red. The colour is fairly fast to light.

ANNALINE is an artificially prepared calcium sulphate used by paper manufacturers.

ANNATTO is the pulpy part of the seeds of *Bixa orellana.* It is produced chiefly in Cayenne and Martinique, and is imported in dry cakes or pulpy masses of a peculiar odour. In India it is used to a considerable extent for dyeing pink or salmon colours on silk or cotton, and, in conjunction with safflower, for oranges and scarlets. It contains a colouring matter, *bixin*, which is now mainly used for colouring butter, cheese, and varnishes.

Material dyed with annatto yields a bright blue colour on spotting with strong sulphuric acid.

ANTHRACENE—

$$C_{14}H_{10} = C_6H_4 \underset{C\,H}{\overset{C\,H}{\diagdown}} C_6H_4.$$
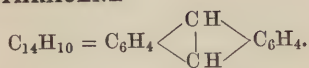
This substance was discovered by Dumas and Laurent in the highest boiling fraction of coal tar. The yield of hydrocarbon is about 0·3 per cent. of the amount of tar operated on. Another source of anthracene is the tar obtained in the manufacture of illuminating gas from petroleum residues when the latter is dropped on to red-hot pumice.

Preparation.—The "green grease" of the heavy portion of the coal-tar distillate becomes semi-solid on standing, owing to the deposition of crystalline bodies. The latter are separated by filtration in bags, which are eventually hot pressed. As the liquid portion still contains some anthracene, it is re-distilled and again separated as above.

The pressed cakes, which contain 25 to 40 per cent. anthracene, are finely ground and purified by agitating in iron vessels with petroleum spirit. The insoluble hydrocarbon is sublimed by passing steam at 230° C. over the melted substance. The sublimed anthracene contains 50 to 60 per cent. of the pure substance. The impurities are *carbazol* (10 to 12 per cent.), *phenanthrene, naphthalene, pyrene, chrysene, acridine,* and high-boiling *phenols.*

The substance is used in this impure state for oxidising into *anthraquinone.* If a purer product be required, Perkin's method of purification is resorted to. The crude substance is distilled with a mixture of potassium carbonate, caustic potash, and lime. The *carbazol* and phenols are thus retained, some other substances are destroyed, hydrogen is evolved, and the distillate, after separating *phenanthrene* by washing with petroleum spirit, leaves a very pure anthracene. All kinds of crude anthracene may be purified by this method.

A peculiar paraffin having, like anthracene, a high melting point and only sparingly soluble in petroleum spirit, generally passes through the purification processes unaltered, and is consequently present in the refined anthracene.

Properties. — Anthracene crystallises in beautiful white scales, having a splendid violet fluorescence which is not visible in gaslight. The melting point is 213° C., and the substance boils just above 260° C. The crystals are sometimes yellow, owing to the presence of *crysogene,* but are bleached on exposure to sunlight, the anthracene simultaneously undergoing a molecular change and decreasing in solubility.

It is sparingly soluble in alcohol and ether, but readily soluble in hot benzol.

On oxidation by means of chromic acid, or manganese dioxide and sulphuric acid, *anthraquinone,* $C_6H_4 \underset{C\,O}{\overset{C\,O}{\diagup\diagdown}} C_6H_4$, is produced.

Strong nitric acid produces the same substance, together with *dinitroanthraquinone.*

Concentrated sulphuric acid converts anthraquinone into two isomeric disulphonic acids.

Chlorine and bromine readily attack anthracene, forming substitution and addition products. Perkin treated anthracene with chlorine on a manufacturing scale, and obtained the crystallised compound *dichloranthracene,* $C_{14}H_8Cl_2$. This substance combines with Nordhausen sulphuric acid, forming a bright green solution which contains a sulphonic acid of dichloranthracene. The latter substance, on heating with sulphuric acid, evolves sulphur dioxide, and a disulphonic acid of anthraquinone is formed—

$$C_{14}H_6Cl_2(H_2SO_3)_2 + H_2SO_4$$
$$= C_{14}H_6O_2(SO_3H)_2 + 2HCl + SO_2.$$
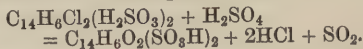
Estimation of Anthracene.—H. Bassett [*] has devised the following method, which differs slightly from the ordinary course of procedure in that nitric acid is used, the author claiming that the end product (which is more or less brown in colour by the ordinary process) is a pure yellow substance, even when obtained from inferior samples. The percentage of anthracene in a sample of the commercial product is determined by oxidising it to anthraquinone by means of chromic acid, dissolving the product in sulphuric acid and precipitating with water; the associated impurities are either destroyed during the oxidation or are converted into sulphonic acids soluble in water.

One grm. of anthracene is introduced, with 45 c.c. of glacial acetic acid, into a flask connected with a reversed condenser and heated to boiling; a solution of 15 grms. of chromic acid in 10 c.c. of acetic acid and 10 c.c. of water is then added drop by drop to the boiling solution during a period of two hours, and the product is boiled for two hours longer and allowed to stand overnight. The product is diluted with 400 c.c. of water, allowed to stand for three hours, filtered, washed with cold water only, and dried on the filter in the water-oven. The quinone is then transferred to a flask with the aid of a funnel having a short and wide neck, and a glass rod, using a small wash bottle containing 45 c.c. of glacial acetic acid to rinse the filter paper, rod, and funnel. 2·5 c.c. of chromic acid solution, and 10 c.c. of ordinary pure nitric acid, of specific gravity 1·42, are then added, after which the mixture is boiled for an hour, using reversed condenser. Next morning the product is diluted with 400 c.c. of water, allowed to stand for three hours,

* *Chem. News,* vol. lxxiii., pp. 178-179.

filtered, washed first with cold water then with boiling 1 per cent. alkali, and finally with hot water. The quinone is then washed into a flat dish, dried at 100°, and heated for ten minutes on a water-bath with ten times its weight of pure concentrated sulphuric acid. It is then left all night to absorb moisture in a tray of water covered with a glass plate, diluted, filtered, washed with water, boiling alkali and hot water, and finally dried and weighed.

The same author [*] states that only pure acetic acid, crystallising at 62° F., should be used, and that the oxidising mixture should not be more than 15 days old.

Anthracene ($C_{14}H_{10}$) forms on oxidation anthraquinone ($C_{14}H_8O_2$). 178 parts of anthracene yield on oxidation 208 parts of anthraquinone.

In connection with anthracene testing, B. Nickels [†] states that pure anthracene and most of the hydrocarbons connected with it in the crude state, when examined with the spectroscope, afford clear and continuous spectra free from absorption bands. Certain substances, however, also present with it in that state, possessing very high fusing points, exhibit deep and broad absorption bands. The former bodies do not affect the crystallisation of anthraquinone, as found by the oxidation test; but the latter seriously interfere with that property, and afford the so-called objectionable "amorphous particles," which occur in greater or less quantity in the anthraquinone obtained as above by the chromic acid oxidation.

A few grains of the sample to be examined are placed in a test-tube, a little benzol added, and warmed to dissolve the anthracene. The mixture is made up to about 6 c.c. with benzol, and filtered to remove water.

The spectroscope is focussed, and the tube of anthracene solution brought into close proximity with the adjusted slit of the spectroscope.

On looking through the solution with a good back light, absorption lines, if present, are seen as fine bars crossing the spectrum.

Estimation of Paraffin in Crude Anthracene. — Heusler and Herde [‡] proceed as follows :—2 grms. of the substance in a flask of 150 c.c. capacity are treated with 25 c.c. of fuming nitric acid, added drop by drop. The flask should be kept cool by means of ice water, then allowed to stand at the ordinary temperature until all the anthracene is dissolved, after which it is heated in the water-bath until the paraffin melts. After cooling, the liquid is filtered through an asbestos filter, and the paraffin on the filter washed with fuming nitric acid until the filtrate dissolves in water without any turbidity. The washing

* *Chem. News*, 1899, p. 157.   † *Ibid.*, vol. xli., p. 52.
‡ *Journ. Soc. Chem. Ind.*, 1895, p. 828.

is then continued with water until the filtrate is neutral. Finally, the paraffin is washed with alcohol and dissolved in warm ether, and the filtrates collected. After evaporation of the solvents, the residual paraffin is dried until of constant weight.

ANTHRACENE BLUE S *v.* ALIZARIN BLUE S.

ANTHRACENE BLUE W B (B.). An anthracene derivative. *Hexaoxyanthra-quinone,*

$$C_6H(OH)_3 \underset{CO}{\overset{CO}{<}} {>} C_6H(OH)_3$$
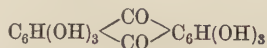
1891. Probably identical with *brilliant alizarin cyanine 3 G* (By.). Blue-black paste, insoluble in water. Soluble in alcohol with a red colour, having a yellow fluorescence. In concentrated H_2SO_4, violet-blue solution, with brownish-red fluorescence.

Application. — A mordant dye. Dyes chrome - mordanted *wool*, *silk*, or *cotton* greenish-blue. With alum mordant, gives blue shades. Mark W G gives the greenest shades, W B navy blue shades, W N somewhat redder shades, and W R much redder shades.

ANTHRACENE BLUE W G (B.). Probably isomeric with the above. 1891. Blue-black paste, soluble in boiling water with a violet-blue colour. In concentrated H_2SO_4, red-brown solution.

Application.—As anthracene blue W B. With chrome mordant greenish - blues are produced. With alum mordant pure blues.

ANTHRACENE BLUE W R (B.). Probably isomeric with anthracene blue W B and W G. 1891. Black-brown paste, insoluble in water. Soluble in alcohol with a red colour, having a yellow fluorescence. In concentrated H_2SO_4, violet-blue solution, with brownish-red fluorescence.

Application.—As anthracene blue W B. Gives dark blue shades with chrome mordant. Violet shades with alum.

ANTHRACENE BROWN (B.) (By.) (M.) (B.A. Co.). *Alizarin brown* (M.), *Anthragallol.* An anthracene derivative, *Tri oxyanthra-quinone,* being isomeric with anthrapurpurin, flavopurpurin, and purpurin. Constitution—

$$C_6H_4 \underset{CO}{\overset{CO}{<}} {>} C_6H(OH)_3.$$ 1877.
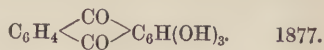
Anthracene Brown Powder. — The sodium salt of the above. Dark brown paste or powder, the former insoluble, the latter soluble in water. In caustic soda, greenish - blue solution. In concentrated H_2SO_4, brownish-red solution; precipitates as brown flocks on dilution.

Application.—A mordant dye. Gives with chromium, drab to dark brown shades; with aluminium, yellowish - browns; with iron, black-browns. *Wool dyeing.* — Used only

with chromium mordant. Applied in a bath slightly acidified with acetic acid. Largely employed, and produces extremely permanent colours. *Silk dyeing.*— Used with aluminium and iron, as well as with chromium mordant. *Cotton dyeing.*—Not much employed, but gives very good results.

ANTHRACENE CHROME BLACK F, F E, 5 B (C.). 1899. Acid mordant dyes, producing with chrome mordant very fast blacks.

ANTHRACENE DARK BLUE (B.).
Application.—A mordant dye. Produces dark indigo shades on chrome-mordanted *wool.*

ANTHRACENE GREEN *v.* COERULEÏN.

ANTHRACENE RED (S.C.I.) (By.) An azo compound. *Sodium salt of*

$$Orthonitro\ benzidine\!<\!{Salicylic\ acid.\atop Alpha\text{-}naphthol\ sul\text{-}\atop phonic\ acid\ N\,W.}$$

1892. Brownish-red powder, soluble with difficulty in water with a red colour. In concentrated H_2SO_4, carmine-red solution, giving a brownish-red precipitate on dilution.
Application.—An acid dye, which forms compounds with metallic mordants. Dyes chrome-mordanted *wool* in an acid bath a red shade, fast to milling and light.

ANTHRACENE VIOLET *v.* GALLEÏN.

ANTHRACENE YELLOW B N (C.) *v.* CHROME YELLOW D (By.).

ANTHRACENE YELLOW C (C.). An azo compound. 1892. Yellowish-brown powder. Soluble in water or alcohol with brownish-yellow colour. Concentrated H_2SO_4 gives a violet solution with evolution of HCl. On dilution reddish-violet ppt., changing to greenish-yellow.
Application.—An acid dye, forming lakes with mordants. Dyes unmordanted or chrome-mordanted *wool* yellow from an acid bath, producing shades fast to light and (with chrome mordant) fast to milling.

ANTHRACENE YELLOW G G (C.). An azo compound. 1892. Greenish-yellow powder. Soluble in water or alcohol with greenish-yellow colour. Concentrated H_2SO_4, brownish-red solution, on dilution changes to purplish-brown.
Application.—An acid dye, forming lakes with mordants. Same as anthracene yellow C, giving much greener (less brown) shade.

ANTHRACENE YELLOW PASTE (By.). An oxy ketone derivative. *Dibrom dioxymethylcumarine.* 1889. Dirty white paste, very slightly soluble in water. In caustic soda, brownish-yellow solution. In concentrated H_2SO_4, brownish-red solution with evolution of HCl. On dilution light yellow ppt.
Application. — A mordant dye. Dyes chrome-mordanted *wool* greenish-yellow.

ANTHRACITE *v.* COAL.

ANTHRACITE BLACK B (C.). *Phenylene black* (P.). An azo dye.

$$Alpha\text{-}naphthylamine\!<\!{Alpha\text{-}naphthylamine\atop disulphonic\ acid.\atop Diphenylmetaphenyl\text{-}\atop ene\ diamine.}$$

1889. Black powder, giving violet solution in water. In concentrated H_2SO_4, black solution giving greenish-black ppt. on dilution.
Application.—An acid dye. Gives blacks fairly fast to milling when dyed on *wool* from an acid bath. Faster to milling when saddened with fluorchrome.

ANTHRAGALLOL *v.* ANTHRACENE BROWN.

ANTHRAPURPURIN. *Isopurpurin. Alizarin G D* (B.), *Alizarin RX* (M.), *Alizarin 3RF* (L.), *Alizarin SC* (B.A.Co.), *Alizarin SX* (B.), *Alizarin SX extra* (By.). An anthracene derivative. *Tri oxyanthraquinone,*

$$C_6H_3(OH)\!<\!{CO\atop CO}\!>\!C_6H_2(OH_2)_2$$
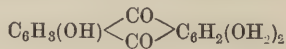
1873. Brownish-yellow (usually 20 per cent.) paste insoluble in cold water, slightly soluble in boiling water. NaOH; blue-violet solution, bluer than alizarin. In concentrated H_2SO_4, cherry-red solution, orange-yellow ppt. on dilution. The dry substance melts at 300° C.
Application.—A mordant dye. Applied in exactly the same way as alizarin, but producing slightly yellower shades (see also ALIZARIN).

ANTHRAQUINONE, $C_6H_4\!<\!{CO\atop CO}\!>\!C_6H_4.$

This substance is formed by the oxidation of anthracene (*q. v.*). It sublimes in shining yellow needles, melting at 273°. Anthraquinone is soluble in hot benzene and in nitric acid. It is a very stable compound, not easily oxidised.

ANTHRAQUINONE BLACK (B.). 1899. A sulphide colour probably allied to *Vidal black.*

ANTICHLOR. This term is applied to any substance which is used to remove free chlorine adhering to the fibres of linen, cotton, and wood pulp after bleaching with hypochlorite.

For this purpose *sodium hyposulphite* (*q.v.*) is largely employed. Its action depends on the fact that in the presence of chlorine, sulphuric acid and sodium chloride are formed. Both substances thus produced are easily removed by washing.

The following substances have also been used :—*Calcium sulphide*, made by boiling milk of lime with sulphur; *stannous chloride* in hydrochloric acid, the free acid being afterwards neutralised with sodium carbonate ; hydrogen peroxide.

ANTIDOTES FOR POISONS commonly employed in Industry.

In all cases of poisoning the safest plan is to immediately administer an emetic consisting of two tablespoonfuls of mustard in one pint of warm water. A scruple (1·25 grm.) of sulphate of zinc in warm water may be used as an emetic. *After the contents of the stomach have been discharged,* the following antidotes may be given :—

POISONS.	ANTIDOTES.
Oil of Vitriol or *Sulphuric Acid*, . . . Muriatic Acid or *Hydrochloric Acid*, . . . Aqua Fortis or *Nitric Acid*, ... Aqua Regia, ... Oxalic Acid, ...	Give *Chalk, Bicarbonate of soda, Whiting, Carbonate of Magnesia,* or *Plaster* scraped from a wall, powdered and stirred up in a small amount of water. Afterwards give milk, white of egg, or sweet oil.
Caustic Soda, ... ,, Potash, ... ,, Ammonia, ... Potassium Carbonate, ... Sodium Carbonate, ... ,, Silicate, ...	Give *warm water* to produce vomiting, then *dilute vinegar* or *lemon juice,* followed by large draughts of milk or some sweet oil.
Prussic Acid or *Hydrocyanic Acid*, . . . The Cyanides, ... The Sulphocyanides, ... Oil of Bitter Almonds, ... Nitrobenzol, ...	*Pour cold water* upon the head, apply *mustard to the soles of the feet,* keep the patient awake by shaking.
Arsenic and its Compounds, ... White Arsenic, ... Fowler's Solution, ...	The *emetic* may contain a tablespoonful of *salt* besides *mustard;* then follow with *sweet oil, milk,* or *butter.* *Dialysed iron* or *ferric hydrate* (precipitated from ferric chloride by slight excess of ammonia and filtered) may follow the emetic.
Soluble Oxalates, ... Oxalic Acid, ...	Give *Chalk, Whiting, Magnesia,* or *Plaster* in water, or *Lime water,* and then castor oil.
Carbolic Acid, ...	Give *Flour* and *Water.*
Sugar of Lead or *Lead Acetate*, . . . Lead Compounds, ... Barium Compounds, ...	Give *Epsom Salts* or *Glauber's Salt* at once, and afterwards an *emetic* of *zinc sulphate* if obtainable, or mustard.
Corrosive Sublimate or *Mercuric Chloride*, . *Nitrate of Mercury*, ...	Give *plenty* of *milk* or *white of egg* in water ; then flour and water.
Silver Nitrate, ...	Administer *common salt* dissolved in water *at once ;* then afterwards a *mustard emetic,* followed by draughts of milk.
Iodine, ...	Give *gruel, arrowroot,* and *starch paste.*
Chromic Acid, ... Chromates, ... Chrome Colours, ...	Give *chalk mixed with water.*

POISONS.	ANTIDOTES.
Tartar Emetic, ...	Give *warm water* to cause vomiting, then *doses* of *strong tea* or *decoction* of *bark.*
Ether, ... Petroleum, ... Benzol, ... Strong Alcohol, ... Fruit Essences, ... Chloroform, ... Chloral Hydrate, ...	Apply *cold water* to the *head, plenty* of *fresh air, keep the patient awake,* employ artificial respiration.
Laudanum, ... Morphine, ... Opium, ...	Give *strong coffee, keep the patient awake* by means of flips with a towel or shaking.

For *gaseous nitrogen oxides* use *vinegar* or *small quantities* of dilute *acetic acid* as strong as can be taken.

In *every instance* of *suspected poisoning* at once give the mustard emetic mentioned above, then employ the antidote (except with silver nitrate, give common salt first, and with lead or barium compounds give Glauber's salts first).

ANTIFEBRIN *v.* ACETANILID.

ANTIMONY, Sb = 120. Antimony usually occurs native in small quantities, but in Sarawak, in Borneo, large masses are found. Combinations of the element with arsenic and sulphur are its principal sources. Antimony is tri- and penta-valent. It resembles phosphorus and arsenic in some respects ; but it also has metallic properties. Both the element and its compounds are poisonous.

Antimony forms a bluish-white crystalline brittle mass of 6·8 specific gravity. It is a constituent of many important alloys, and some compounds of the substance are used in pharmacy and dyeing.

Antimony forms the following compounds with oxygen :—

Antimony trioxide, Sb_2O_3	{ Antimonious acid, $HSbO_2$.
Antimony tetroxide, Sb_2O_4	{ Hypoantimonious acid, $H_2Sb_2O_5$.
Antimony pentoxide, Sb_2O_5	{ Antimonic acid, $HSbO_3$. Metantimonic acid, $H_4Sb_2O_7$.

Antimony Trioxide, antimonious oxide, Sb_2O_3, is found native, and can be prepared by heating antimony in air. It may also be obtained by mixing hot solutions of antimony trichloride, and sodium carbonate. It is a greyish-white powder, which becomes temporarily yellow on heating ; it melts at a red heat, and may be sublimed out of contact with air. It is very sparingly soluble in water, is insoluble in nitric acid, but dissolves in hydrochloric, sulphuric, and tartaric acid, and in caustic alkalies.

The application of antimony salts in dyeing is limited to the salts of antimony trioxide, and these are employed exclusively in the dyeing and printing of cotton and linen. Their usefulness is based on the fact that tannic acid forms a lake with antimony trioxide, which is insoluble in tannic acid. Faster colours are obtained with antimony tannate than with tannic acid alone. Antimonious oxide is used in the preparation of *tartar emetic.*

Sb_2O_3 dissolves in an alkaline solution of glycerin. In this form it is used as a mordant for cotton. The solution should be free from sulphide of antimony, otherwise the colours lose brilliancy. The addition of hydrochloric acid precipitates the yellow sulphide of antimony if present.

Antimony Pentoxide, Sb_2O_5, is formed by gently igniting metantimonic acid. It is a yellow amorphous substance soluble in hydrochloric acid. By continued ignition the substance loses oxygen, and the compound Sb_2O_4 (antimony tetroxide) is produced.

Antimonious Acid, $HSbO_2$.—On the addition of caustic alkalies or carbonates of the alkalies to solutions of antimony salts, antimonious hydroxide ($HSbO_2$) is precipitated, and this is converted into antimony trioxide on boiling. The acid is soluble in excess of caustic potash or soda. It acts both as an acid and as a base. In the latter capacity it is both mono- and trivalent ; in the monovalent condition it is considered to

4

be combined with oxygen, forming the mono-valent radical *antimonyl* (SbO).

The salts which antimony forms with acids, when soluble in water, redden blue litmus, and possess a very disagreeable metallic taste. They are dissociated by water, antimony tri-oxide being thrown down, and an acid salt remaining in solution.

Sulphuretted hydrogen precipitates from acidified solutions of the salts orange-red antimonious sulphide (Sb_2S_3), which is soluble in alkaline sulphides.

Antimonic Acid, $HSbO_3$, exists in two modifications, distinguished by different basicities. Antimonic acid obtained by the action of nitric acid on the metal or by adding an acid to potassium antimonate is a white powder almost insoluble in water. It gives rise to a series of neutral salts having the general formula $MSbO_3$.

Metantimonic Acid, $H_4Sb_2O_7$, is obtained by the decomposition of antimony penta-chloride by water. It is more soluble in water than antimonic acid, and is di-basic, forming unstable salts of the general formula $M_4Sb_2O_7$ and $M_2Sb_2O_5$. The alkaline metantimonates are crystalline, whereas the antimonates are amorphous. The acid met-antimonate of potassium, $H_2K_2Sb_2O_7 \cdot 6H_2O$, is used as a test for sodium compounds, with which it forms a precipitate having the com-position $NaHSbO_3 . 3H_2O$.

Antimony Trichloride, $SbCl_3$, is obtained by the action of chlorine upon the metal or by dissolving antimony trioxide in hydro-chloric acid. It is a light yellow deli-quescent mass, and is dissociated by water according to the equation—

$$SbCl_3 + H_2O = SbOCl + 2HCl.$$
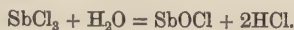
Antimony Fluoride, $SbFl_3$, is obtained by dissolving antimony trioxide in hydrofluoric acid. The salt forms colourless rhombic pyra-mids, which are deliquescent; by dilution with water it is not decomposed ; on evapo-rating the solution, without excess of hydro-fluoric acid, a basic fluoride is obtained. Antimony fluoride attacks glass and metals, except lead and platinum. It is kept in wooden casks.

Antimony fluoride forms crystalline double salts with one, two, or three equivalents of the fluorides, chlorides, and sulphates of the alkalies.

Antimony Sodium Fluoride, SbF_3NaF, has been brought into the market by R. Koepp & Co., in Oestrich a. Rh. (Germany), under the name of *double antimony fluoride*. It crystallises in triclinic prisms, and is readily soluble in water ; 100 parts of cold water dissolve 63 parts of the salt, and 100 parts of hot water 166 parts. The solution can be diluted without dissociation. It has a slightly acid reaction, and corrodes glass and

metals. The salt contains the equivalent of 66 per cent. Sb_2O_3, and 658 grms. are equi-valent to 1000 grms. of tartar emetic.

Analysis.—Gottlieb Stein [*] gives the fol-lowing methods of analysis :—*Qualitative*— On the addition of potassium ferrocyanide solution to the solution of double fluoride of antimony, no indication of iron should appear ; on the addition of barium chloride solution containing hydrochloric acid, there should be no precipitate of barium sulphate. *Quanti-tative*—0·5 grm. of double fluoride of antimony is dissolved in hot water, and then a drop of phenolphthaleïn solution and ammonia are added, until the liquid shows an alkaline reaction. The antimony oxide is rapidly precipitated, and, after washing three times by decantation, transferred to a filter, washed, dried at 110° C., and weighed ; it is then washed again, dried at 110° C., and weighed.

The commercial article is almost chemically pure.

Antimony Fluoride and Ammonium Sulphate, in the form of a double salt, $SbF_3(NH_4)_2SO_4$ (*Antimony salt*), and several similar compounds, are sold as substitutes for *tartar emetic*. The substance forms white crystals easily soluble in water (14 parts dis-solve in 10 parts of water). The aqueous solution has a strong acid reaction, and cor-rodes glass and metals. Compared with tartar emetic it contains about 10 per cent. more available antimony. The solution is un-affected by dilution.

According to W. P. Thompson's patent [†] for preparing compounds of antimony fluoride and alkaline sulphates having the general formula $2SbF_3 . M_2SO_4$, and containing a larger amount of antimony than any similar double salt hitherto known, antimony oxide is dissolved in hydrofluoric acid, and the requisite quantity of alkaline sulphate stirred into the warmed solution. On cooling, the double salt crystallises out.

Antimony and Potassium Double Oxalate, $SbK_3(C_2O_4)_3 + 4H_2O$.—This body crystallises in fine needles, and is easily soluble in cold water. The solution, however, quickly decomposes, an insoluble basic oxalate of antimony being precipitated. The substance is prepared by dissolving antimony trioxide in acid potassium oxalate.

It has been stated that antimony double oxalate, although containing only 25 per cent. Sb_2O_3, can replace an equal weight of tartar emetic which contains 43½ per cent. of anti-mony oxide, as it yields its antimony more readily to the fibre. This is not generally conceded.

Analysis.—The antimony in oxalate of anti-mony and other antimony salts may be deter-mined as in tartar emetic. Hart's process,

* *Chem. Zeit.*, 1887, No. 84.
† *Journ. Soc. Chem. Ind.*, 1893, p. 785.

however, does not give satisfactory results. In such cases it is preferable to titrate an alkaline solution of the salt with $\frac{N}{10}$ iodine.

M. B. Setlick [*] adds a standard solution of caustic soda to a solution of a weighed quantity of the salt until a slight turbidity makes its appearance. The amount of alkali used indicates the *free oxalic acid* contained in the sample. Phenolphthaleïn (on which antimony oxide itself has no action) is now added along with sufficient alkali to produce a red coloration. This gives the amount of *antimony oxide* present. Finally, in order to estimate the percentage of *alkali* a fresh portion is precipitated with ammonia, filtered, the filtrate evaporated to dryness, calcined, and the residue of alkaline carbonate titrated with $\frac{N}{1}$ sulphuric acid. This simple process invariably gives good results.

Tartar Emetic, $(SbO) KC_4H_4O_6 + \frac{1}{2}H_2O$, *potassium antimony tartrate*, is obtained by boiling antimonious oxide with cream of tartar. It forms octahedral crystals which lose water on exposure to the air. The crystals dissolve in about 15 parts of water at 15° C. and in about 2 parts of boiling water. The solution has a disagreeable metallic taste and is very poisonous. It has an acid reaction, and dissociates on standing, forming an insoluble basic antimony tartrate. The crystals of tartar emetic contain 43·4 per cent. Sb_2O_3; the commercial product, which is in lumps or fine crystals, generally contains 43 per cent.

The substance is subject, however (especially if purchased in the powdered form), to adulteration either with cheaper antimony salts or with zinc sulphate and other substances; it may contain the required quantity of antimony without being genuine tartar emetic. Oxalate of antimony and the double fluoride of ammonium and antimony are frequently used as adulterants.

Analysis.—*Antimony* as *antimonious oxide* may be readily estimated by titrating an alkaline solution with $\frac{N}{10}$ iodine and starch. W. B. Hart's process,[†] which consists in adding an excess of a solution of bleaching-powder and titrating with $\frac{N}{10}$ arsenious acid, can be recommended. 0·5 grm. of the sample is dissolved in about 50 c.c. of warm water and cooled. 20 c.c. of a 10 per cent. solution of sodium bicarbonate and 25 c.c. of a 2 per cent. solution of bleaching-powder are added, and the liquid well stirred with a glass rod. If sufficient bleaching-powder has been added, a drop of the liquid will now produce a blue colour with potassium iodide and starch paper. Decinormal sodium arsenite (4·95 grms. of As_2O_3 per litre) is then run in until a drop

of the liquid ceases to give any coloration with the iodide and starch paper (*v.* THIO-SULPHATE). The strength of the bleaching-powder solution used to oxidise the antimony is determined, when the amount of chlorine expressed in terms of arsenite is readily calculated. 1 c.c. of $\frac{N}{10}$ arsenite = 0·006 grm. of Sb or 0·0072 grm. of Sb_2O_3.

Example.—0·5 grm. of tartar emetic with sodium bicarbonate and 25 c.c. of chloride of lime required 7·5 c.c. of $\frac{N}{10}$ arsenite. 25 c.c. of chloride of lime alone required 36·5 c.c. of $\frac{N}{10}$ of arsenite. Therefore, chlorine equivalent to 29 c.c. of arsenite was used in oxidising the antimonious oxide present.

$$\therefore \frac{0 \cdot 0072 \times 29 \times 100}{0 \cdot 5} = 41 \cdot 76 \,°/_{o} \text{ of } Sb_2O_3.$$

Antimony may be also accurately estimated by precipitating it as Sb_2S_3, and weighing it as such, or distilling the sulphide in a flask with hydrochloric acid, and collecting the hydrogen sulphide evolved in a known volume of $\frac{N}{10}$ arsenite solution and estimating the excess of arsenite with thiosulphate (*Schneider*). *Pure tartar emetic* contains 43·4 per cent. of Sb_2O_3. Some samples in the market contain *more* than that amount, owing to the presence of ammonium antimony fluoride. If this salt is present, ammonia will be evolved on boiling with caustic soda.

Oxalate in tartar emetic may be detected and estimated, if necessary, by precipitating the antimony as sulphide in an acid solution. The filtrate is boiled to expel hydrogen sulphide, a slight excess of ammonia is then added, and the liquid made slightly acid with acetic acid, and treated with calcium chloride solution, whereby calcium oxalate is precipitated (*v.* OXALIC ACID).

Antimony Lactate has been patented [*] for the same applications in dyeing and printing for which the other antimony salts are used. The salt is said to be not crystallisable, very soluble in water, and not to dissociate.

ANTIMONY SALT *v.* ANTIMONY (ANTIMONY FLUORIDE).

ANTINONNIN (By.) *v.* VICTORIA ORANGE.

APOLLO RED (G.). *Orchil substitute N extra* (C.). An azo compound.

Paranitraniline — Alpha-naphthylamine disulphonic acid D.

1887. Brown powder, giving brownish-red solution in water. In concentrated H_2SO_4, magenta-red solution, no change on dilution.

Application.—An acid colour. Dyes *wool* orchil red from an acid bath.

AQUA FORTIS *v.* NITRIC ACID.

AQUA REGIA. *Nitrohydrochloric acid.* This is a mixture of 1 volume of nitric acid

---

[*] *Chem. Zeit.*, No. 72, 1886.
[†] *Journ. Soc. Chem. Ind.*, 1884, p. 294.

[*] C. N. Waite, U.S. Patent 341,294.

with 3 or 4 volumes of hydrochloric acid. The liquid gradually becomes yellow on standing or heating, due to the formation of free chlorine and nitrosyl chloride (NOCl). This mixture readily dissolves gold and platinum.

$$HNO_3 + 3HCl = NOCl + Cl_2 + 2H_2O.$$

ARCHIL v. ORCHIL.

ARCHIL RED v. ORCHIL RED.

ARNICA YELLOW (G.). A tetrazo compound derived from *stilbene*. 1892. Brown powder, giving brownish-yellow solution in water. In NaOH, red-brown solution. In concentrated H_2SO_4, violet solution. On dilution brown precipitate.

Application.—A direct cotton dye. Dyes unmordanted *cotton* golden-yellow.

ARSENATE OF ALUMINIUM v. ALUMINIUM SALTS.

ARSENATE OF IRON v. IRON (FERRIC ARSENATE).

ARSENATE OF SODA v. SODIUM ARSENATE.

ARSENIC, As 75.—Arsenic occurs native in small quantity mixed with silver, nickel, cobalt, and iron, and in combination with oxygen, sulphur, or one of the three latter metals. Metallic arsenic is of very limited use in commerce. It is usually prepared by heating the ores with metallic iron, and collecting the sublimed element, or in the case of the oxide (As_2O_3), distilling with charcoal. Compounds of arsenic give off the characteristic odour of garlic when heated on charcoal. If a small piece of charcoal be ground up with the suspected substance, placed in a hard glass bulb tube, and heated in the Bunsen flame, a dark ring of metallic arsenic will be deposited in the cool part of the tube, if an appreciable amount of the element be present. This part of the tube may be cut off, the stain dissolved in a little nitric acid, and the usual tests applied after volatilisation of the free nitric acid by evaporation. If a little dry sodium acetate be heated together with an arsenic compound in a glass tube, cacodyl, a compound immediately recognised by its disagreeable odour, is evolved.

Reinsch's Test.—A piece of clean copper foil becomes coated with a film of arsenic when immersed in a hydrochloric acid solution of a compound of arsenic. If the strip of metal be washed, dried, and heated in a small glass tube, a ring of white crystalline oxide of arsenic will be formed in the cool portion of the tube.

Sulphuretted hydrogen precipitates a yellow sulphide of arsenic, As_2S_3, from hydrochloric acid solutions of arsenic compounds. The yellow precipitate is soluble in nitric acid, ammonium sulphide, or in ammonium carbonate.

For the detection of arsenic in textile fibres v. TEXTILE FIBRES, ANALYSIS OF.

Arsenic Acid v. ARSENIC OXIDE.

Arsenic Oxide, As_2O_5. *Arsenic anhydride.* If arsenic or arsenious oxide be oxidised by means of concentrated nitric acid or chlorine, a solution of arsenic acid results, which on evaporation leaves crystals having the composition $H_3AsO_4 + \frac{1}{2}H_2O$. The crystals lose their water of crystallisation at 100°, and at a higher temperature suffer further loss of water, *pyro-arsenic acid,* $H_4As_2O_7$, and later *meta-arsenic acid,* $HAsO_3$, being formed. At a red heat meta-arsenic acid decomposes, giving off the remaining water, and arsenic anhydride is produced.

Arsenic oxide is a white glassy solid, having an acid reaction. It fuses at a red heat and deliquesces in air. It is soluble in water, and is used as an oxidising agent in the manufacture of rosaniline, &c. Arsenious anhydride is also employed in calico printing as a substitute for tartaric acid.

Arsenious Acid v. ARSENIOUS OXIDE.

Arsenious Oxide, As_2O_3. *White Arsenic, Arsenious acid,* "Arsenic." This substance is prepared by roasting the ores of arsenic in furnaces, the white vapours or "soot" being condensed in long chambers. The sublimate is impure and a second volatilisation is always necessary.

The purified arsenious oxide is an amorphous glassy substance, which, on keeping, becomes opaque and crystalline. The vitreous form is more soluble in water than the crystalline modification. It is very soluble in glycerine; Jackson (*C. N.,* vol. xlix., p. 258) states that a glyceryl arsenite is produced.

The oxide, although acid to litmus and soluble in water, does not apparently form a true arsenious acid in aqueous solution. It is very poisonous.

Arsenious oxide is used for fixing aniline colours—*e.g.,* aniline blue; and in the preparation of arsenic acid and various pigments —*e.g., Scheele's green, Schweinfurt green,* &c. It is also employed in calico printing, either dissolved in a solution of sodium carbonate or in glycerine.

Analysis.—*Calcium sulphate* and *carbonate,* which are often present in commercial arsenious oxide, remain as a non-volatile ash when a portion of the substance is ignited on platinum foil.

The percentage of As_2O_3 may be determined by practically the same method as that described for standardising the $\frac{N}{10}$ arsenite of soda v. CALCIUM CHLORO-HYPO-CHLORITE. 2 grms. of the sample are dissolved in water containing about 5 grms. of sodium carbonate, and diluted to 500 c.c. 100 c.c. (= 0·2 grm.) are withdrawn, neutralised with a little pure hydrochloric acid, 25 c.c. of a saturated solution of sodium

bicarbonate added, and the liquid titrated with $\frac{N}{10}$ iodine. 1 c.c. $\frac{N}{10}$ iodine = 0·00495 grm. As_2O_3.

Arsenite of Soda (*Standard solution*) v. CALCIUM CHLORO-HYPOCHLORITE.

ARSENIC IN FABRICS v. TEXTILE FABRICS.

ASSISTANTS. These bodies are employed, chiefly in wool dyeing, as additions to the mordant-bath or dye-bath, their function being, as their name implies, to assist the fixation of the mordant or dyestuff. The chief mordant assistants are *acid potassium tartrate* (cream of tartar), *acid potassium oxalate* (binoxalate of potash), and *tartaric, oxalic, lactic, sulphuric,* and (rarely) *hydrochloric acids.* Their action varies. In some cases the organic acids or salts prevent too rapid dissociation of the mordant—*e.g.*, cream of tartar with alum mordant. In other cases they act as reducing agents—*e.g.*, lactic acid with bichromates ; while in other cases again they increase the activity of the mordant—*e.g.*, sulphuric acid with bichromates.

The assistants used in the dye-bath are somewhat numerous. In applying the acid colours, *sulphuric acid* and *sodium sulphate* are the usual additions ; but *sodium bisulphate, sodium acetate, ammonium sulphate,* and *acetate,* and *acetic acid* are also employed. *Soap* and "*boiled-off liquor*" (v. SILK) are used in silk dyeing. In applying the "*direct dyes*" to cotton, *sodium chloride, sulphate, phosphate,* and *carbonate* are used ; and in the tartar emetic "fixing bath," frequently used in the process of dyeing cotton with basic dyes on tannin mordant, *sodium* or *ammonium chloride* is a valuble assistant.

ATLAS ORANGE (Br. S. & Sp.) v. ORANGE II.

ATLAS RED (Br. S. & Sp.). An azo compound.

Primuline base — Metatoluylene diamine.

1889. Dark red powder, giving a brownish-red solution in water.

Application.—A direct cotton dye. Dyes unmordanted *cotton* terra-cotta-red in an alkaline bath. May be produced as an ingrain colour on the fibre by dyeing with primuline, azotising, and developing with metaphenylene diamine.

AURAMINE O, I, II, CONCENTRATED (B.) (S.C.I.) (M.) (G.). A diphenylmethane derivative. *Hydrochloride of amidotetramethyldiamidodiphenylmethane.* The various marks represent different degrees of purity and concentration. 1883. Sulphur yellow powder, soluble in water or alcohol with a yellow colour. Insoluble in alkaline solutions. In concentrated H_2SO_4, colourless solution, yellow on dilution. Is decomposed on boiling with dilute acids.

Application.—A basic dye. Dyes *silk* or tannin mordanted *cotton* greenish-yellow. Much used for staining paper.

AURAMINE G (B.) (S.C.I.) (G.). A ditolylmethane derivative. *Hydrochloride of amidodimethyldiamidodiorthotolylmethane.* 1892. Yellow powder, soluble in water or alcohol. Reactions and application similar to auramine.

AURANTIA. *Imperial yellow.* A nitro compound. *Ammonium or sodium salt of hexanitrodiphenylamine.* 1873. Orange-yellow powder or red-brown crystals. When heated on platinum foil, burns with deflagration. Soluble in water with orange-yellow colour. In concentrated H_2SO_4, pale yellow solution, precipitating on dilution. Is a strong acid, decomposing carbonates, and forming well crystalline metallic salts.

Application.—An acid dye. Used principally for dyeing an orange colour on leather. Employed also in preparation of photographic dark-room screens.

AUREOLIN (D. & H.) v. PRIMULINE.

AUREOSIN. *A chlorinated fluoresceine.* 1876. No longer in use.

Application as eosin.

AURINE. *Rosolic acid.* A triphenyl carbinol derivative. *Trioxytriphenyl carbinol.* Commercial aurine is a mixture of aurine, oxyaurine, methylaurine, and pseudorosolic acid ($C_{20}H_{26}O_4$), the latter being the chief constituent. 1859. Yellowish-brown lumps, with lustrous fracture. Insoluble in water, soluble in alcohol. Soluble in dilute alkali. In concentrated H_2SO_4, yellow solution, precipitating on dilution.

Application. — Used in colouring spirit varnishes and lacquers.

Yellow coralline is the sodium salt of commercial aurine. Metallic, green, lustrous lumps, soluble in water with a red colour. In alcohol, magenta-red solution. In concentrated H_2SO_4, yellow solution, precipitating on dilution.

Application as aurine.

AURINE R v. CORALLIN.

AUROTIN (Clayton Co.). A triphenyl carbinol derivative. *Sodium salt of tetranitrophenolphthaleïn.* 1889. Orange-yellow powder, soluble in water or alcohol with a deep yellow colour.

Application.—An acid colour, and a mordant dye. Dyes unmordanted *wool* orange-yellow, or chrome or alum-mordanted wool a greener yellow, in an acid (acetic) bath.

AZALEINE. An old name for impure magenta.

AZALIN (M.). A mixture of *quinolin red* and *quinolin blue,* used for rendering photographic plates orthochromatic.

AZAMIN 4 B v. BENZOPURPURIN 4 B.

AZARIN R (M.). An azo compound, containing hydroxyl groups. The *ammonium*

bisulphite compound of the body obtained by combining *beta-naphthol* with azotised *diamido oxysulphobenzide.*

$$SO_2 \left\langle \begin{array}{l} C_6H_3(OH) . N = N - C_{10}H_6(OH) \\ C_6H_3(OH) . N = N - C_{10}H_6(OH) \end{array} \right. + 2NH_4 . HSO_3$$
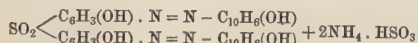
It resembles azarin S in reactions and method of application.

AZARIN S (M.). An azo compound, containing hydroxyl groups. *Ammonium salt of dichlorphenolhydrazo beta-naphthol sulphonic acid.*

$$C_6H_3(OH)Cl_2 . NH . N \left\langle \begin{array}{l} SO_3NH_4 \\ C_{10}H_6(OH) \end{array} \right.$$

1883. Yellow paste, similar in appearance to alizarin, but smelling of sulphurous acid. Slightly soluble in water. Becomes violet on treatment with alkali. In concentrated H_2SO_4, magenta-red solution, which gives reddish-brown ppt. on dilution.

Application.—A mordant dye. Used in *cotton* dyeing and calico printing with alum mordant, being applied in the same manner as alizarin. The colours are very permanent, and are somewhat bluer than alizarin.

AZINDONE BLUE *v.* INDAMINE.

AZINE BLUE (D.) *v.* INDULINE.

AZINE GREEN G B (L.). An azonium derivative. *Dimethylamido phenylamido phenylphenonaphthazonium chloride.* 1889. Dark green powder, soluble in water or alcohol. In concentrated H_2SO_4, brown solution, becoming green on dilution.

Application.—A basic dye. Dyes tannin-mordanted *cotton* dark green.

AZINE GREEN S (L.). *Sodium salt of sulphonic acid of azine green G B.* 1890. Green powder, soluble in water but not in alcohol. In concentrated H_2SO_4, blue-violet solution, becoming brown, and finally blue-green on dilution.

Application.—An acid dye. Gives a dark blue-green shade on *wool* or *silk* in an acid bath. Fast to light.

AZINE SCARLET G EXTRA (M.). A yellowish-red basic dyestuff, belonging to the safranine group.

AZO ACID BLACK B, G, R, T L, 3 B L (M.). Acid dyes employed in *wool* dyeing.

AZO ACID BLUE B (M.). An acid blue allied to *Victoria violet 4 B S* (M.), used in *wool* printing and dyeing.

AZO ACID BLUE 4 B, 6 B (By.). Acid colours, dyeing a pure blue shade on *wool* from an acid bath.

AZO ACID BROWN (By.). An acid colour, dyeing very level brown shades on *wool* from an acid bath.

AZO ACID CARMINE B (M.). An acid dye for *wool.*

AZO ACID MAGENTA B (M.) and **G** (M.). Acid crimson dyes, producing very level shades on *wool* in an acid bath.

AZO ACID RUBINE (D.) *v.* FAST RED C (B.).

AZO ACID RUBINE 2 B (D.) *v.* FAST RED D (B.).

AZO ACID VIOLET 4 R (By.) An acid colour, dyeing *wool* reddish-violet from an acid bath.

AZO ACID YELLOW (Ber.) *v.* AZO YELLOW (M.).

AZO BLACK O (Ber.) *v.* BLUE BLACK B (B.).

AZO BLACK BLUE (O.). A tetrazo colour.

$$Tolidine \left\langle \begin{array}{l} Amidonaphthol \ disulphonic \\ acid \ H. \\ Metaoxydiphenylamine. \end{array} \right.$$
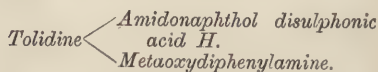
1890. Grey-brown powder, soluble in water, with a blue-violet colour. In concentrated H_2SO_4, blue solution, ppt. on dilution.

Application.—A direct *cotton* dye. Dyes unmordanted cotton from an alkaline salt bath a dark violet-blue, fast to washing, alkali, and acid, but not to light.

AZO BLUE (By.) (Ber.) (L.) (Lev.). A tetrazo compound.

$$Tolidine \left\langle \begin{array}{l} Alpha-naphthol \ sulphonic \\ acid \ N W. \\ Alpha-naphthol \ sulphonic \\ acid \ N W. \end{array} \right.$$
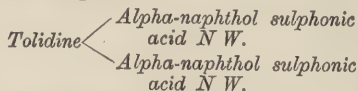
1885. Bluish-black powder, giving a violet solution in water. In concentrated H_2SO_4, blue solution, violet ppt. on dilution.

Application.—A direct *cotton* dye. Dyes unmordanted cotton grey-violet from a soap bath.

AZO BORDEAUX (By.). *Buffalo rubine* (Sch.). An azo compound.

Alpha-naphthylamine—Alpha-naphthol disulphonic acid R G.

1884. Brown powder, soluble in water, with a magenta-red colour. In concentrated H_2SO_4, blue solution, becoming crimson on dilution.

Application.—An acid dye. Dyes *wool* and *silk* red from an acid bath.

AZO BROWN O (M.) *v.* NAPHTHYLAMINE BROWN (B.).

AZO CARDINAL G (Ber.). An acid dye, giving very level shades on *wool.*

AZO CARMINE B (B.). *Rosinduline 2 B* (K.) *Sodium salt of phenylrosinduline trisulphonic acid.* 1888. Red-brown powder, slightly soluble in water, with a blue-red colour. In concentrated H_2SO_4, green solution, red ppt. on dilution with water.

Application.—An acid dye. Gives a fine blue-red on *wool* or *silk* in an acid bath.

AZO CARMINE G (B.). *Rosarin* (P.). *Sodium salt of phenylrosinduline disulphonic acid.* 1888. Glistening crystalline paste, only slightly soluble in water. Reactions and application as azo carmine B.

AZO CARMINE B X POWDER AND G PASTE (B.). Acid dyes similar to above.

AZO CHROMINE (G.). An azo compound. *Amidophenol azo pyrogallol.* 1893.

Application.—A mordant dye. Gives yellow shades on chrome-mordanted *wool*.

AZO COCCINE 7 B (Ber.). *Cloth red G* (By.). A disazo compound.

Amidoazo benzene — Alpha-naphthol monosulphonic acid N W.

1883. Brown powder, sparingly soluble in water, with a red colour. In concentrated H_2SO_4, blue-violet solution; brownish-red ppt. on dilution.

Application.—An acid colour. Dyes *wool* and *silk* bluish-red from an acid bath.

AZO COCCINE G (Ber.). *Tropaeolin OOOO.* An azo compound.

Aniline — Alpha-naphthol sulphonic acid N W.

1887. Reddish-brown powder, slightly soluble in water. In concentrated H_2SO_4, magenta-red solution, unchanged on dilution.

Application.—An acid colour, dyeing *wool* brick-red from an acid bath.

AZO COCCINE 2 R (Ber.). *Double scarlet R* (Lev.). An azo compound.

Xylidine — Alpha-naphthol monosulphonic acid N W.

1882. Reddish-brown powder, soluble in water. In concentrated H_2SO_4, magenta-red solution, giving brownish-red ppt. on dilution.

Application.—An acid colour. Dyeing *wool* and *silk* red from an acid bath.

AZO COCHINEAL (By.). An azo compound.

Orthodianisidine — Alpha-naphthol disulphonic acid Sch.

Red powder, slightly soluble in water. In concentrated H_2SO_4, dark red solution, becoming yellowish-red on dilution.

Application.—An acid colour. Dyes very level pink and scarlet shades on *wool* from an acid bath.

AZO COLOURS ON COTTON. The sulphonated azo colours used in wool dyeing have little or no affinity for cotton. Azo compounds are therefore produced direct upon cotton by impregnating the fibre with one of the constituent parts, and then passing the cotton thus prepared into a solution of the necessary combining body.

The constituent parts of an azo colour are (*a*) a phenol or amine, and (*b*) a diazotised base, and the process (introduced by Messrs. Read Holliday in 1880) usually consists in saturating the fibre with an alkaline solution of a phenol, drying, and developing in a neutral solution of the diazotised base.

In calico printing—rarely in dyeing—the fibre may be impregnated with a paste containing the whole of the colour ingredients and the colour developed by steaming (Graessler & Schmidt, 1890).

Substances employed in the process:—

(*a*) **Phenols.**—Very few are used, practically only—

Beta-naphthol.
     ,, R and D (M.L. & B.).
Alpha-naphthol.
Resorcinol.

Of these, *beta-naphthol* is much the most important. *Amines* are not used.

Padding or Grounding.—The intensity or depth of shade of the ultimate colour depends entirely upon the strength of the grounding or padding solution, which for moderately intense colours may contain

20 to 25 parts	beta-naphthol.	
36 ,, 45 ,,	caustic soda sol. 36° Tw.	
60 ,, 75 ,,	Turkey-red oil.	
1000 ,,	water.	

The grounded cotton rapidly becomes dark coloured on exposure to light, and the colour should therefore be at once developed; but by adding to the naphthol bath some mild reducing agent, such as tartar emetic, this defect, which is due to oxidation, is greatly diminished.

The padded material must be dried immediately and at a temperature not exceeding 60° C.

Paranitraniline Red.—This is the most important colour of the series, being largely used as a substitute for Turkey red. It is produced by preparing the cotton as above and developing the colour by working in a solution of diazotised paranitraniline, which may be prepared as follows:—Stir to a paste 10 lbs. paranitraniline with 2 gallons water; then add 2 gallons hydrochloric acid (35° Tw.) and 6 gallons water. After mixing well add 5½ lbs. sodium nitrite dissolved in 2 gallons water. Dilute to 200 gallons and neutralise with sodium acetate. The colour is produced instantaneously on passing the padded cotton into this solution, the cotton being subsequently washed, dried, and soaped.

Azophor Red P N (M.L. & B.) is *paranitro diazobenzene chloride.*

$$C_6H_4{\overset{NO_2}{\underset{}{\diagdown}}}N = N - Cl$$
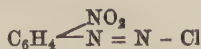
It is sold as a brownish-yellow powder which when dissolved in water produces a solution of diazotised paranitraniline base on addition of caustic soda. It therefore yields paranitraniline red on cotton prepared with beta-naphthol.

By the use of "naphthol R" (M.L. & B.) instead of beta-naphthol, somewhat bluer reds are produced, and the substitution of Para soap P N (ricinoleate of ammonia) for

(b) Aromatic Bases.

BASE.	FORMULA.	COLOUR PRODUCED WITH β-NAPHTHOL.
Aniline, ...	$C_6H_5 . NH_2$	Orange-yellow.
Paratoluidine, . . .	$C_6H_4 {<}^{CH_3 \ (1)}_{NH_2 \ (4)}$ . . .	Yellow-orange.
Metanitraniline, . . .	$C_6H_4 {<}^{NH_2 \ (1)}_{NO_2 \ (3)}$ . . .	Orange ; or in conjunction with copper salts, brown.
Nitroparatoluidine, . .	$C_6H_3 {-}^{CH_3 \ (1)}_{\substack{NH_2 \ (4) \\ NO_2}}$ . . .	Orange.
Nitro-orthotoluidine,. .	$C_6H_3 {-}^{CH_3 \ (1)}_{\substack{NH_2 \ (2) \\ NO_2}}$ . . .	Orange-red.
Paranitraniline, . . .	$C_6H_4 {<}^{NH_2 \ (1)}_{NO_2 \ (4)}$ . . .	Red ; or in conjunction with copper salts, brown.
Azophor red P N (M.L.&B.),	A diazotised paranitraniline .	Do.
Nitrosamine red (B.A.S.F.),	$C_6H_4 {<}^{N {<}^{NO}_{Na} \ (1)}_{NO_2 \ (4)}$ . .	Do.
Amidoazo benzene, . .	$C_6H_5 - N = N - C_6H_4 . NH_2$	Crimson.
Beta-naphthylamine, . .	$C_{10}H_7NH_2 \ (\beta)$ . . .	Crimson ; or in conjunction with copper salts, brown.
Blue red O (M.L.&B.), (Nitrophenitidine).	$C_6H_3 {-}^{O(C_2H_5)}_{\substack{NH_2 \\ NO_2}}$ . . .	Blue-crimson.
Orthoamidoazo toluene, .	$C_6H_4 {-}^{CH_3}_{N=N-C_6H_3} {-}^{CH_3 \ (1)}_{NH_2 \ (2)}$	Claret-red or garnet.
Alpha-naphthylamine, .	$C_{10}H_7 . NH_2 \ (\alpha)$ . . .	Blue shade of claret-red.
Benzidine, ...	$C_6H_4 . NH_2$ $\mid$ $C_6H_4 . NH_2$ . . .	Purplish-brown.
Tolidine, ...	$C_6H_3 {-}{<}^{CH_3}_{NH_2}$ $\mid$ $C_6H_3 {-}{<}^{NH_2}_{CH_3}$ . . .	Purplish-brown (redder).
Dianisidine, . . .	$C_6H_3 {<}^{O(CH_3)}_{NH_2}$ $\mid$ $C_6H_3 {<}^{NH_2}_{O(CH)_3}$ . . .	Blue (in conjunction with copper salts).
Azophor blue D, . . .	An azotised dianisidine . .	Do.
Azo black base (M.L.&B.), .	. . . . . .	Black.
Azo black base O N, (M.L.&B.).	. . . . . .	Black.

(c) Other Substances used in Ingrain Dyeing.

Substance.	Use.
Sulphated oil (Turkey-red oil), ...	Employed with beta-naphthol, &c. Makes most colours much brighter.
Para acid (Ricinoleic acid) (M. L. & B.), . . Para soap P N (Ricinoleate of ammonia), . . (M. L. & B.). Para soap R N (Ricinoleate of soda), . . . (M. L. & B.). Oxyoleic acid A (Schmitz & Toenges), . .	Used instead of sulphated oil in special cases.
Sodium nitrite, ...	Employed for diazotising bases.
Ice, ...	Used for cooling certain diazo solutions.
Acetate of soda, ... Acetate of ammonia, ... Chalk, ...	Employed for neutralising diazo solutions.
Aluminate of soda, ...	Used with nitrosamine red.
Alkaline copper chloride, ... Chromic acid, ...	Used in developing blues and browns.
Potassium sulphite, ... Ammonium persulphate, ... Oxalic acid, ... Sodium hypochlorite, ... Stannous chloride, ... Magnesium chloride, ...	Used as resists or discharges in printing processes.

Turkey red oil somewhat increases the brilliancy of the colour.

Nitrosamine Red (B.A.S.F.) is a yellowish paste of the composition—

$$C_6H_4 < {\substack{N < {\substack{NO \\ Na}} \\ NO_2}} \quad \text{(paranitrophenyl nitrosamine).}$$
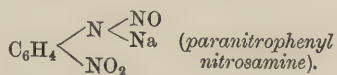
It produces diazotised paranitraniline on treatment with dilute hydrochloric acid.

Azo Oranges, Yellows, Crimsons, Claret Reds, &c., are obtained in a similar manner to paranitraniline red, but by the use of other bases as shown by the tabulated list given above.

Azo Browns are produced by the action of copper salts on the colour formed by beta-naphthol with *paranitraniline, metanitraniline, or beta-naphthylamine.* The copper salt is employed in alkaline solution and is usually added to the naphthol prepare.

Azo Blues are produced by combination of beta-naphthol (or naphthol D (M.L.& B.)) with *dianisidine* (or *azophor blue* (M.L.& B.)) and subsequent treatment with chloride of copper and chromic acid.

AZO CORINTH (O.). An azo disazo compound.

Naphthionic acid >Resorcinol.
Tolidine <Amidophenol sulphonic acid III.
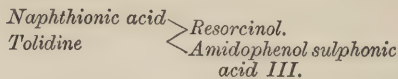
1892. Blackish-brown powder, giving a red-brown solution in water. In concentrated H_2SO_4, blue-violet solution, giving a brownish-red ppt. on dilution.

Application.—A direct cotton dye. Dyes unmordanted *cotton* brownish-violet from a soap bath.

AZO DIPHENYL BLUE v. INDULINE.

AZO DYES. This term is applied to a very numerous group of dyes prepared by modifications of one general reaction — *the diazo reaction*—discovered by P. Griess in 1858. Diazo compounds are formed when primary amines of the aromatic series are treated with *nitrous acid*—*e.g.*,

$$C_6H_5 . NH_2 . HCl + HNO_2$$
Aniline hydrochloride.
$$= C_6H_5 . N : N . Cl + 2H_2O.$$
Diazobenzene chloride.
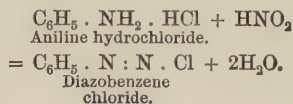
The free diazo compounds (e.g., C_6H_5 . N : N . OH) are not yet known, and the *salts* (e.g., diazo benzene chloride) are extremely unstable and even explosive, and are usually only prepared as dilute aqueous solutions. They are colourless compounds.

Diazo compounds readily combine with *phenols* or *amines*, producing bodies which possess tinctorial properties; in short, the azo dyes.

(1) C_6H_5 . N : N . Cl + C_6H_5 . OH
        Diazo benzene chloride.   Phenol.

= C_6H_5 . N : N . C_6H_4 . OH + HCl ;
        Oxyazo benzene.

or (2) C_6H_5 . N : N . Cl + C_6H_5 . NH_2
                                        Aniline.

= C_6H_5 . N : N . C_6H_4 . NH_2 + HCl.
        Amidoazo benzene.

Thus two groups of azo dyes may be distinguished, the *oxyazo* and the *amidoazo* dyes; the former greatly preponderating in number and importance.

Oxyazo compounds are usually insoluble in water, and the commercial dyestuffs are mostly sodium salts of *sulphonic acids* of these bodies.

C_6H_5 . N : N . C_8H_4 . OH.
        Oxyazo benzene.

C_6H_5 . N : N . $C_6H_3{<}^{OH}_{SO_3Na}$.
        Oxyazo benzene sodium sulphonate
        (acid yellow).
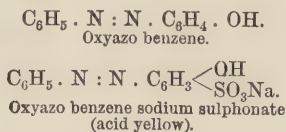
Amidoazo dyes, being primary aromatic amines, may be diazotised and combined with phenols or amines, exactly in the same manner as the simpler amines; thus *amidoazobenzene* (C_6H_5 . N : N . C_6H_4 . NH_2) may produce *benzene azobenzene azonaphthol*

$(C_6H_5$. N : N . C_6H_4 . N : N . $C_{10}H_6$. OH).
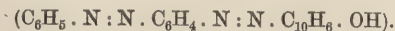
Azo colours may thus contain one, two, or more azo groups.

As indicated above, the azo dyes usually contain sulphonic acid groups, and this is a characteristic of acid dyes (*q.v.*). One large group of the azo sulphonic acids, however, have the special property of dyeing cotton and other vegetable fibres without the aid of a mordant. This property appears to reside only in those dyes which contain two azo groups symmetrically placed as regards the connecting body. These dyes are known as the *Congo*, *Benzidine*, or *Direct cotton* colours (*v.* the latter).

Insoluble azo dyes (e.g., *paranitraniline red*) are frequently used as dyestuffs for cotton, being actually formed on the fibre (*v.* AZO COLOURS ON COTTON).

AZO EOSIN (By.).   An azo compound.

*Orthoanisidine — Alpha-naphthol mono-
            sulphonic acid N W.*

1885.   Red powder, soluble in water.   In concentrated H_2SO_4, carmine-red solution, giving brownish-red ppt. on dilution.

Application.—An acid colour.   Dyes *wool* eosin pink or red from an acid bath.

AZO FLAVIN (B.) (D.) *v.* AZO YELLOW.

AZO FUCHSINE B (By.).   An azo compound.

*Toluidine — Dioxynaphthalene mono-
            sulphonic acid Sch.*

1889.   Black-brown powder, giving a bluish-red solution in water.   In concentrated H_2SO_4, violet solution, becoming bluish-red on dilution.

Application.—An acid and an acid mordant colour.   Dyes *wool* magenta-red from an acid bath; when developed with $K_2Cr_2O_7$, produces a black.

AZO FUCHSINE G (By.).   An azo compound.

*Sulphanilic acid — Dioxynaphthalene mono-
            sulphonic acid Sch.*

1889.   Reddish-brown powder, giving bluish-red solution in water.   In concentrated H_2SO_4, violet solution, becoming bluish-red on dilution.

Application—An acid and an acid mordant colour, giving slightly less blue shades than azo fuchsine B; when developed with $K_2Cr_2O_7$, produces a black.

AZO FUCHSINE G N EXTRA (By.).   A similar product, possessing great colouring power.

AZO GALLEINE (G.).   *Hydrochloride of amidodimethylaniline azo pyrogallol.*   1895. Greenish-brown paste.   Yellow-brown solution in water and alcohol.   Concentrated H_2SO_4, reddish-brown solution, which is unchanged on dilution.

Application. — A mordant dye.   Gives purple shades on chrome-mordanted *wool*.

AZO GREEN (By.).   *Tetramethyldiamidotriphenylcarbinol azo salicylic acid.*   1888. Dark green paste, slightly soluble in water. In concentrated H_2SO_4, reddish-brown solution, which ppts. reddish-brown flocks on dilution.

Application.—Dyes chrome-mordanted *wool* green.   Little used.

AZO GRENADINE L, S (By.).   Easily levelling acid red dyes.

AZO MAUVE B (O.).   A tetrazo compound.

Tolidine${<}^{Amidonaphthol\,disulphonic\,acid\,II.}_{Alpha\text{-}naphthylamine.}$

1890. Bronzy-black powder, giving a red-violet solution in water. In concentrated H_2SO_4, blue solution, giving a blue-violet ppt. on dilution.

Application.—A direct cotton dye. Dyes unmordanted *cotton* blackish blue-violet from a soap bath.

AZO MAUVE R (O.). Is the *benzidine* derivative corresponding to azo mauve B. It is similar to the latter in appearance, reactions, and method of application.

AZO NIGRINE (G.). An azo compound.

$$Disulphophenol\ azo \atop naphthylamine\ \} - Beta\text{-}naphthol.$$

1891. Brownish-black paste, giving blue-black solution in water. In concentrated H_2SO_4, greenish-black solution, red ppt. on dilution.

Application.—An acid colour. Dyes *wool* brownish-black from an acid solution.

AZO ORANGE R (D. & H.). An azo compound containing four azo groups.

$$Tolidine \Big< \begin{array}{l} Naphthionic\ acid. \\ Dioxydiphenyl\ methane. \\ Naphthionic\ acid. \end{array}$$
$$Tolidine \Big<$$

1893. Red powder soluble in water with a brown-yellow colour. In concentrated H_2SO_4, blue solution, giving a dark grey ppt. on dilution.

AZO ORCHIL R (Ber.) Brownish-red powder easily soluble in water or alcohol to claret-red solution. Concentrated H_2SO_4, claret-red solution, which becomes yellower on dilution.

Application.—An acid dye, giving brownish-red shades on *wool.*

AZO ORSEILLIN (Ber.)(By.). An azo dye.

$$Benzidine \Big< \begin{array}{l} Alpha\text{-}naphthol\ monosulphonic \\ \quad acid\ N\ W. \\ Alpha\text{-}naphthol\ monosulphonic \\ \quad acid\ N\ W. \end{array}$$

1883. Dark violet paste, giving a reddish-violet solution in water. In concentrated H_2SO_4, blue solution; violet ppt. on dilution.

Application.—A direct cotton dye. Dyes unmordanted *cotton* brownish-red from a soap bath.

AZOPHOR BLUE D (M.) *v.* Azo Colours on Cotton.

AZOPHOR RED PN (M.) *v.* Azo Colours on Cotton.

AZOPHOSPHINE (L.) A basic yellow dye.

AZOPURPURIN 4 B (D. & H.). A direct cotton colour producing bright red shades.

Application.—A direct cotton colour. Dyes unmordanted *cotton* orange from a salt bath.

AZO RED A (C.) *v.* Palatine Red (B.).

AZO RUBINE A (C.) *v.* Fast Red C (B.).

AZO RUBINE S (Ber.) *v.* Fast Red C (B.).

AZO TURKEY RED (O.) *v.* Azo Colours on Cotton.

AZO VIOLET (By.) (Ber.) (L.) (Lev.). An azo compound.

$$Dianisidine \Big< \begin{array}{l} Naphthionic\ acid. \\ Alpha\text{-}naphthol\ mono\text{-} \\ \quad sulphonic\ acid\ N\ W. \end{array}$$

1886. Black-blue powder, giving a reddish-violet solution in water. In concentrated H_2SO_4, blue solution, which precipitates on dilution.

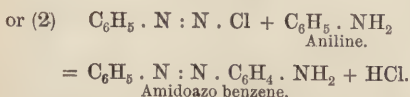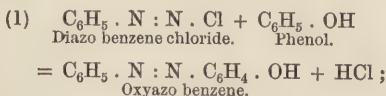*Application.*—A direct cotton dye. Dyes unmordanted *cotton* blue-violet from a soap bath.

AZO YELLOW (S.) (S.C.I.) (K.) *Azo yellow M* (D. & H.), *Azo flavin* (B.) (D.), *Azo acid yellow* (Ber.), *Indian yellow* (By.), *Indian yellow G* (C.), *Helianthin* (G.), *Citronine* (P.). Produced by action of nitric acid on *diphenylamine* yellow. 1880. Yellow powder, giving greenish-yellow solution in water. In concentrated H_2SO_4, magenta-red solution; on dilution, brown ppt.

Application.—An acid colour. Dyes *wool* and *silk* yellow from an acid bath.

AZULINE. *Azurine.* An obsolete blue basic dye obtained by the action of aniline on aurine.

AZURINE *v.* Azuline.

AZURINE (B.). An oxazine compound. *Chloride of dimethylphenylammoniumoxyphenoxazine carboxylic acid.* 1890. Black paste, soluble in hot water. In concentrated H_2SO_4, indigo-blue solution, becoming magenta-red on dilution.

Application.—A mordant dye. Dyes chrome mordanted *wool* a violet-blue shade.

B

BABLAH or NEBBAH is the fruit of several species of *Acacia.* It is principally obtained from East Indies (*Acacia arabica*) and Egypt (*Acacia nilotica*). The fruits contain 15 to 20 per cent. tannin (ellagitannic acid) and some brown colouring matters. Bablah is employed in black dyeing.

BARBERRY BARK is the principal member of a very interesting group of natural dyes, which are peculiar in containing colouring matters of a *basic* character. They are, therefore, applied in conjunction with tannin mordant in the same way as magenta and other basic coal-tar colours.

Origin.—This bark is the root bark of the *Berberis vulgaris*, or common barberry, a plant of very wide distribution. It contains a colouring principle (*berberine*) which has the composition $C_{20}H_{17}NO_4$, and which dyes

unmordanted *wool* a bright yellow colour. It does not dye unmordanted *cotton*.

Recently *Berberis oetnensis*, which grows abundantly in Cyprus, has been examined by A. G. Perkin,[*] who finds that it also contains *berberine*. The same investigator has also found *berberine* in the root bark of *Toddalia aculeata*,[†] a shrub found in India and Ceylon, and in *Evodia meliœfolia*, a Chinese dye plant.

Berberine also exists in the root of *Loscinium fenestratum*, and is the only natural basic yellow dye known.

BARIUM, Ba = 137. Barium occurs in nature chiefly in the form of *heavy spar*, $BaSO_4$, and as *witherite*, $BaCO_3$. The metal itself has only scientific interest. The soluble salts of barium are poisonous.

Barium Chloride, $BaCl_2$, is used for precipitating sulphuric acid in analysis. It is a white, crystalline, easily soluble salt.

Barium Chromate, $BaCrO_4$, is obtained by precipitating the solution of a barium salt with chromate or bichromate of potash. It has a light yellow colour; is insoluble in water and acetic acid, but soluble in nitric and hydrochloric acids; and is used as a yellow pigment, under the name of "yellow ultramarine," in calico-printing. It offers the advantage that it is not blackened in an atmosphere containing sulphuretted hydrogen, but it does not give such full colours as chrome yellow.

Barium Peroxide, BaO_2. Barium peroxide is manufactured from the nitrate by igniting the latter in pots, the salt fusing and being decomposed, solid *baryta* (BaO) being ultimately left. A stream of purified air is afterwards passed over the disintegrated baryta, contained in iron trays at a dull red heat. It forms a greyish-white porous mass. Dilute acids dissolve barium peroxide, forming a barium salt and peroxide of hydrogen—

$$BaO_2 + 2HCl = H_2O_2 + BaCl_2.$$
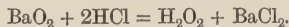
On heating barium peroxide above 400° C., oxygen is evolved and barium oxide remains.

Barium peroxide is used for direct bleaching, and for the preparation of pure oxygen and of hydrogen peroxide.

Barium Sulphate (*blanc fixe, permanent white*), $BaSO_4$. Natural barium sulphate (*heavy spar*) is used in different degrees of purity and fineness as a loading for paper, and as a carrier for dyes in the colouring of papers.

Blanc fixe is an artificial product obtained by the action of sulphuric acid on barium chloride solution.

It occurs in commerce in the form of a fine powder or lumps, and, on making into a paste, mixes well with soluble colours.

Barium Sulphocyanide, or Thiocyanate, $Ba(CNS)_2$, is prepared, according to V. Holbing,[*] by boiling Prussian blue for a short time under pressure with a small excess of barium sulphide and some free sulphur, in the form of spent (gasworks) oxide. The mass is lixiviated, treated with carbon dioxide to remove the remaining barium sulphide as carbonate, and filtered. The filtrate is evaporated and allowed to crystallise, the product being pure enough for use by dyers without further treatment. The salt crystallises with 2 molecules of water, and is very soluble and deliquescent. It is used for the preparation of sulphocyanides, which are used as mordants in textile printing.

Barium Tungstate. This substance is used in printing to produce opaque and dull effects. The substance may be precipitated on the fibre by printing sodium tungstate upon fabrics previously printed with ground colours, and afterwards passing through a solution of barium chloride.[†]

BARK *v.* Quercitron Bark.

BARWOOD *v.* Redwoods (insoluble).

BARWOOD SPIRITS *v.* Tin Spirits.

BARYTA *v.* Barium Oxide.

BASIC ALUM *v.* Aluminium (Ammonium Alum).

BASIC COLOURS. The basic colours are the salts of organic bases of artificial origin. Their colour-bearing or chromophorous group is contained in the bases, hence the name "basic colours." The bases in the free state are colourless, and their chromogenic character appears only when they combine with acids to form salts. In the dyeing of the various textile fibres the dyestuff salts present in the dye-bath are decomposed; the acid remains in solution, while the colour base combines with an acid already present in or on the fibre, and thus gives rise by chemical action to an insoluble, or sparingly soluble, coloured salt or lake, which forms the dye. In the case of cotton and linen, this acid must be deposited in the fibre by mordanting with tannic acid, Turkey-red oil, &c., whereas the animal fibres act by themselves as acids, hence they are dyed without mordants. Jute behaves like tannin prepared cotton.

All the basic colours have the property of dyeing cotton mordanted with tannin or other acid mordants—*e.g.*, Turkey-red oil or soap—and the same dyestuff always assumes on the different mordants a more or less similar shade. The shade is not materially altered even when the acid mordants are fixed by different metals—*e.g.*, antimony, tin, or aluminium, &c. Hence these dyestuffs are "monogenetic" in character.

[*] *Trans. Chem. Soc.*, 1897, pp. 1, 198.
[†] *Ibid.*, 1895, p. 413.

[*] *Journ. Soc. Chem. Ind.*, 1897, p. 680
[†] *Ibid.*, 1898, p. 921.

Reds.

Acridine Red B, 2 B, 3 B.
,, Scarlet R, 2 R, 3 R.
Azine Scarlet.
Brilliant Rhoduline Red B.
Cerise (Magenta).
Cotton Scarlet G.
Giroflée N.
Grenadine.
Induline Scarlet.
Isorubine.
Janus Red.
· ,, Claret-red.
Magdala Red.
Magenta.
Neutral Red.
New Magenta.
Phenosafranine.
Pyronine B, G.
Rhoduline Red B, G.
Rhodamine B, 3 B, G, 6 G,
S.
Rosolan.
Rosaniline.
Rubine (Magenta).
Russian Red (Magenta).
Safranine.
Safranine Scarlet G.

Oranges and Yellows.

Acridine Orange N O, R extra.
Auramine.
Azophosphine.
Benzoflavine.
Chrysoidine.
Flavinduline.
Homophosphine G.
Janus Yellow R.
Leather Yellow G, R.
New Phosphine.
Phosphine.
Rheonine B.
Tannin Orange R.
Thioflavine T.

Greens.

Acid Green Y Y O.
Azine Green B O, G O.
Benzal Green O, I.
Brilliant Green.
Capri Green G.
China Green.

Diamond Green.
   (*N.B.*—Some Diamond Greens
      are acid colours).
Diazine Green.
Emerald Green.
Ethyl Green.
Imperial Green.
Janus Green B, G.
Malachite Green.
Methyl Green.
Methylene Green.
New Green.
Solid Green.
Victoria Green.

Blues.

Azindone Blue G, R.
Basle Blue 2 B, R, S.
Brilliant Cresyl Blue.
Brilliant Diazine Blue B, 2 B.
Capri Blue G O N.
Cresyl Blue.
Diazine Blue B, B R.
Diphene Blue R
Ethylene Blue.
Fast Acid Blue.
   ,, Blue.
   (*N.B.*—Some Fast Blues are
      acid colours.)
Gentianine.
Glacier Blue.
Helvetia Blue.
Indamine Blue.
Indanil Blue.
Indazine M.
Indigen F, R.
Indoin 2 B, B, R, 2 R.
Indol Blue R.
Indoline.
Indophenin B, extra.
Janus Blue G, R.
Metamine Blue.
Metaphenylene Blue 2 B, B,
   R.
Methylene Blue.
Methylindone B, R.
Muscarine J.
Naphthazurine Blue.
Naphthindone 2 B.
New Blue D, R.
   ,, Fast Blue F, H.
   ,, Indigo Blue F, R.
   ,, Metamine Blue.
   ,, Methylene Blue.
   ,, Victoria Blue.

Night Blue.
Nile Blue A, 2 B, R.
Paraphenylene Blue B, G, R.
Phenylene Blue B, R, M.
Setocyanine.
Setoglaucine.
Setopaline.
Thionine Blue G D.
Toluidine Blue.
Toluylene Blue B, R.
Turquoise Blue.
Vacanciene Blue Paste.
Victoria Blue B, R, 4 R.

Violets.

Amethyst.
Clematine.
Cresyl Fast Violet 2 B, R N.
Crystal Violet.
Cyclamen.
Ethyl Purple 6 B.
Fast Neutral Violet B.
Fuchsine.
Hofmann's Violet.
Methyl Violet.
Neutral Violet extra.
Paraphenylene Violet.
Parma Violet.
Regina Purple.
Rhoduline Violet.
Tannin Heliotrope.
Violamine 3 B, B, R, 2 R.
Violet.

Browns.

Aniline Brown.
Bismarck Brown.
Diazine Brown.
Janus Brown B, R.
Leather Brown 00.
Manchester Brown.
Nut Brown A.
Tannin Brown R.
Vesuvine.

Blacks.

Diazine Black.
Methylene Grey.
New Grey.
Nigramine.

The basic colours vary greatly in their general physical and chemical properties, in their constitution and their chromophors, and, lastly, in the brilliancy and fastness of their shades. A large number, like *magenta, malachite green, rosaniline blue*, and *methyl violet* are derivatives of *triphenylmethane*, and are characterised by the chromophorous group
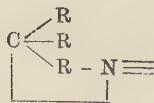
They are distinguished from most other basic colouring matters by superior brilliancy of hue, but this is associated with great fugitiveness. Many of the basic colours, like the *safranines, new blue,* and the *indulines* are azine derivatives, containing the colour-bearing group
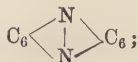
still others, like *phosphine* and *acridine orange,* owe their tinctorial properties to the *phenyl-acridine* radical
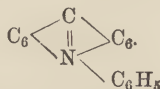
Allied colours, as *methylene blue* and *thioflavine* contain *sulphur* as an essential constituent, and, lastly, *chrysoidine, Bismarck brown, tannin orange,* and the *Janus* dyes are azo colours.

The basic colours are brought into commerce generally as salts of hydrochloric acid, but some are sold as acetates, oxalates, sulphates, nitrates, or as double salts of hydrochloric acid and zinc chloride. The free colour bases are rarely met with.

The basic dyes are sold in powder or crystalline form, or as pastes. Most of them are soluble in water, while all dissolve in alcohol. On addition of the hydroxides or carbonates of the alkalies and alkaline-earths to the solutions, the colour bases are usually thrown down in the free state, most of them being insoluble in water.

BASLE BLUE B B (D. & H.). An azonium base produced by action of *nitrosodiethylaniline hydrochloride upon (2 : 7) ditolylnaphthylene diamine.* 1886. Brown crystalline powder, giving purple solution in water. Concentrated H_2SO_4, greenish-brown solution, which on dilution becomes green, then violet, and finally gives a bluish-violet ppt.

Application.—A basic colour. Dyes *cotton* prepared with tannin and tartar emetic bright blue ; *wool,* blue in neutral bath.

BASLE BLUE B B S (D. & H.) is a sulphonated derivative of the above, and dyes *wool* blue from an acid bath.

BASLE BLUE R (D. & H.). Analogous in composition and properties to Basle blue B B, but produced from *dimethylaniline.* Sold in paste form.

BASLE BLUE R S (D. & H.). Sulphonated derivative of Basle blue R. An acid colour.

BASTOSE v. JUTE.

BAUXITE v. ALUMINIUM (ALUMINATE OF SODA).

BAVARIAN BLUE D B F (Ber.). *Diphenylamine blue, Soluble blue S B and 10 B* (Br. S. & Sp.). A pararosaniline derivative. *Sodium salt of triphenylpararosaniline trisulphonic acid.* 1866. Produced by sulphonating diphenylamine blue. (See also METHYL BLUE (C.).) Dull blue powder. In water, blue solution. Insoluble in alcohol. Concentrated H_2SO_4, yellowish-brown solution, becoming green and then blue on dilution.

Application.—An acid colour. Dyes *wool* or *silk* blue from an acid bath. Also dyes tannin mordanted *cotton.*

BAVARIAN BLUE DSF (Ber.). A pararosaniline derivative. The disulphonic acid corresponding to the above. 1866. (See also METHYL BLUE FOR SILK.) Indigo - blue powder, soluble in water. Concentrated H_2SO_4, as D B F (above).

Application.—An acid dye. Used principally for *silk,* and giving a pure blue shade.

BAVARIAN BLUE SPIRIT SOLUBLE (Ber.) v. DIPHENYLAMINE SPIRIT BLUE.

BENGAL BLUE G v. BENZOAZURIN G (By.).

BENGAL CATECHU v. CATECHU.

BENGAL RED v. ROSE BENGAL.

BENZAL GREEN (O.) v. MALACHITE GREEN.

BENZENE, *Benzol,* C_6H_6, is one of the products of the destructive distillation of coal, and occurs in coal tar. It is a colourless, mobile liquid, possessing an etherial smell, and having a specific gravity of 0·8841 at 15° C. ; it solidifies at about 0° C., melts at 8° C., and boils at 80·5° C. It is very inflammable, and burns with a smoky flame. It is not miscible with water, but mixes in all proportions with alcohol and ether. It freely dissolves sulphur, phosphorus, fats and resins. Benzene, which has the definite formula C_6H_6 must not be confounded with "benzine," the commercial substance obtained in the refining of petroleum, and which is a mixture of several hydrocarbons.

Analysis.—Benzol is usually tested as follows :—

1st. A retort must be employed connected with a Liebig's condenser.

2nd. A thermometer is to be fitted into the retort, the bottom of the bulb of which is to be placed ⅔ inch from the bottom of the retort.

3rd. 100 c.c. of benzol are to be placed in the retort.

4th. Heat is to be applied by the flame of a Bunsen burner.

5th. The distillation must be carried on so that the distillate falls rapidly in separate drops from the end of the condenser.

6th. The temperature is to be allowed to rise to 100° C., the flame is then taken away, and the distillate measured. Similarly the temperature is then carried to 120° C., and the distillate measured, and the measure of these distillations in cubic centimetres gives the percentage of 100° and 120° C. "benzol" respectively.

B. Nickels * estimates the *light hydrocarbons* and *non-nitrifiable substances* in commercial benzols by the method mentioned below.

Carbon bisulphide has a remarkable influence in marking the true character of benzol.

Method of Testing.—Take 300 c.c. benzene and add 35 c.c. of a saturated solution of caustic potash in absolute (methylated) alcohol; subject this mixture to frequent agitation during the space of half an hour. If of 90 per cent. quality, and of London make, the fluid generally becomes pasty or semi-solid from formation of potassium xanthate. This is filtered off, drained, the filter carefully folded, and then gently pressed with a spatula against the sides of the funnel so as to press out the residual benzol. To the benzol so treated is added water in a capacious separating funnel, and the whole agitated for a few minutes. After complete separation of the two layers, the lower stratum of water and alcohol is run off, and the supernatant benzol washed again by agitation with water. The benzol is finally run into a stoppered bottle and agitated with a small quantity of plaster of Paris (gypsum); this effects immediate removal of water held in suspension. The operations are repeated a second time, using 15 c.c. of alcoholic potash. After this purification from carbon bisulphide the benzol is tested by the usual retort method mentioned above, noting the temperature at which the first "drop" falls, and distillate at 84° point. The difference observed will be considerable. First, entire disappearance of alliaceous odours; second, decrease of specific gravity according to the amount of carbon bisulphide originally present; third, disappearance of abnormal boiling point, rising from 80° to 83° for drop, and falling from 25 to 30 per cent. to 6 or 8 per cent. of the 84° point. A standard 90 per cent. benzol was prepared by admixture of pure benzol, specific gravity 0·885, 70 parts; pure toluol, specific gravity 0·771, 30 parts, and which represents the proportion of benzol present in a good 90 per cent. The specific gravity of the mixture is 0·8805. The boiling point, as determined by the ordinary 8-oz. retort method of testing, is as follows :—

* *Chemical News*, vol. lii., p. 170.

		From which it will be seen that the wider the departure of "drop" in distillation from 85·4° the greater will be the quantity of "light hydrocarbons" present, a deduction further confirmed by specific gravities on the light side of 0·8805.
At 85·4° C.,	drop.	
86·2° C.,	5 p. ct.	
86·6° C.,	10 ,,	
87·2° C.,	20 ,,	
87·8° C.,	30 ,,	
88·8° C.,	40 ,,	
89·8° C.,	50 ,,	
91·4° C.,	60 ,,	
93·2° C.,	70 ,,	
96·2° C.,	80 ,,	
102·0° C.,	90 ,,	

Carbon bisulphide may be estimated directly in a solution of the potassium xanthate removed on filtering, by standard copper sulphate solution or computation from decrease of specific gravity.

1 per cent. CS_2 raises the density by 0·0033.
2 ,, ,, ,, 0·0065.
3 ,, ,, ,, 0·0093.

To test this method the following mixture was prepared :—

Pure benzol, ...	63	parts
Pure toluol, ...	27	,,
Light hydrocarbons (sp. gr. 0·760),	8	,,
Carbon bisulphide, . . .	2	,,
	100	,,

The specific gravity of the mixture was 0·879. Tested in the ordinary way by distillation in an 8-oz. retort

It gave—		After treatment with alcoholic potash.	
At 79·0° C.,	drop.	At 82·5° C.,	drop.
84·0° C.,	21 p. ct.	84·0° C.,	5 p. ct.
88·5° C.,	30 ,,	85·0° C.,	10 ,,
87·2° C.,	40 ,,	86·2° C.,	20 ,,
88·5° C.,	50 ,,	87·2° C.,	30 ,,
90·4° C.,	60 ,,	88·2° C.,	40 ,,
92·6° C.,	70 ,,	89·6° C.,	50 ,,
95·6° C.,	80 ,,	91·2° C.,	60 ,,
100·0° C.,	90 ,,	93·3° C.,	70 ,,
		96·7° C.,	80 ,,
		100·0° C.,	90 ,,

After treatment with alcoholic potash, the specific gravity fell to 0·871, indicating CS_2 (removed) and light hydrocarbons (present).

The figures then obtained by distillation (given in the right-hand column) answer to an excellent sample of 90 per cent. benzol, notwithstanding it contained at least 8 per cent. of "light hydrocarbons," or "non-nitrifiable compounds."

BENZIDAM. An old name for ANILINE.

BENZIDINE, $(C_6H_4NH_2)_2 = H_2N - C_6H_4 - C_6H_4 - NH_2$. The starting point of the manufacture of a series of direct cotton colours.

BENZIDINE BLUE. An obsolete blue direct cotton dye similar to benzoazurin.

BENZIDINE RED. An obsolete red direct cotton dye similar to benzopurpurin.

BENZINDAMIN v. INDAMINE.

BENZOAZURINE G (By.) (Ber.) (L.) (Lev.). An azo compound.
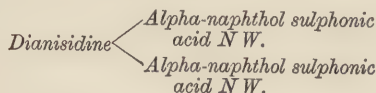
$$\text{Dianisidine} \left\{ \begin{array}{l} \textit{Alpha-naphthol sulphonic} \\ \quad \textit{acid N W.} \\ \textit{Alpha-naphthol sulphonic} \\ \quad \textit{acid N W.} \end{array} \right.$$

1885. Blue-black powder, giving violet solution in water. In concentrated H_2SO_4, blue solution, which precipitates on dilution.

Application.—A direct cotton dye. Dyes unmordanted *cotton* blue from an alkaline bath, the dyed material becoming reddish on heating, but blue again on cooling.

BENZOAZURINE 3 G (By.) (Ber.) (L.). An azo compound.

$$\text{Dianisidine} \left\{ \begin{array}{l} \textit{Alpha-naphthol sulphonic} \\ \quad \textit{acid Cl.} \\ \textit{Alpha-naphthol sulphonic} \\ \quad \textit{acid Cl.} \end{array} \right.$$
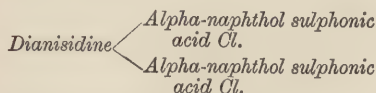
1885. Greyish-black powder, giving blue-violet solution in water; in alcohol, red-violet solution; in concentrated H_2SO_4, blue solution, which gives a violet solution on dilution.

Application.—A direct cotton dye colour. Dyes unmordanted *cotton* blue from an alkaline bath.

BENZOAZURINE R (By.) (Ber.) (L.). A mixture of benzoazurin G and azo blue.

BENZO BLACK - BLUE G (By.) An azo derivative.

$$\text{Benzidine disul-}\atop\text{phonic acid} \left\{ \begin{array}{l} \textit{Alpha-naphthylamine} \\ \quad + \textit{alpha-naphthol} \\ \quad \textit{sulphonic acid N W.} \\ \textit{Alpha-naphthol} \\ \quad \textit{sulphonic acid N W.} \end{array} \right.$$
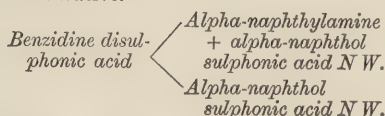
1887. Black powder. Aqueous solution, blue-black. Insoluble in alcohol. Concentrated H_2SO_4, black-green solution, producing black-blue ppt. on dilution.

Application.—A direct cotton dye. Dyes unmordanted *cotton* black-blue from an alkaline bath.

BENZO BLACK-BLUE 5 G (By.) An azo derivative.

$$\text{Benzidine disul-}\atop\text{phonic acid} \left\{ \begin{array}{l} \textit{Alpha-naphthylamine} \\ \quad + \textit{dioxynaphthalene} \\ \quad \textit{sulphonic acid S.} \\ \textit{Dioxynaphthalene} \\ \quad \textit{sulphonic acid S.} \end{array} \right.$$
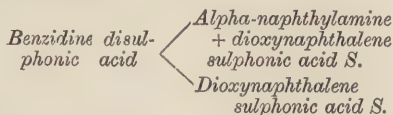
1892. Grey powder, slightly soluble in water, with a black-blue colour. Insoluble in alcohol.

In concentrated H_2SO_4, black-green solution, giving dark green ppt. on dilution.

Application.—As benzo black-blue G, but gives a greener shade.

BENZO BLACK - BLUE R (By.). An azo compound.

$$\text{Tolidine} \left\{ \begin{array}{l} \textit{Alpha-naphthylamine} \\ \quad + \textit{alpha-naphthol} \\ \quad \textit{sulphonic acid N W.} \\ \textit{Alpha-naphthol} \\ \quad \textit{sulphonic acid N W.} \end{array} \right.$$
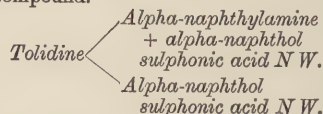
1887. Greyish-black powder, giving a blue-violet solution in water. In alcohol, violet solution. In concentrated H_2SO_4, blue solution, giving bluish-violet ppt. on dilution.

Application.—As benzo black-blue G, but gives more violet colours.

BENZO BLACK - BROWN (By.) 1893. Greyish-black powder. Soluble in water, brown solution, and in alcohol with black-red colour. Concentrated H_2SO_4, violet solution, which on dilution changes to reddish-violet, then reddish-brown, and finally brown.

Application.—A direct cotton dye, applicable to *cotton* or *union material.* The shade produced is dark brown.

BENZO BLACK (B.). Black powder. Aqueous solution, violet; alcohol, slightly soluble. Concentrated H_2SO_4, dull violet-blue colour, which on dilution becomes violet and then blue.

Application.—A direct cotton dye.

BENZO BLUE B B (By.) v. DIAMINE BLUE 2 B.

BENZO BLUE 3 G (By.) v. DIAMINE BLUE 3 B.

BENZO BLUE B X (By.) v. DIAMINE BLUE B X.

BENZO BROWN B (By.). An azo compound, containing four azo groups.

$$\begin{array}{l} \textit{Naphthionic acid} \\ \textit{Metaphenylene} \\ \quad \textit{diamine} \\ \textit{Naphthionic acid} \end{array} \left\{ \begin{array}{l} \textit{Metaphenylene diamine.} \\ \\ \textit{Metaphenylene diamine.} \end{array} \right.$$
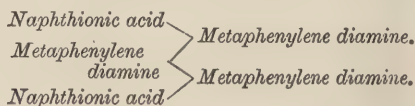
1887. Brown-black powder, soluble in water, with reddish-brown colour; slightly soluble in alcohol. In concentrated H_2SO_4, dirty violet solution, giving brown ppt. on dilution.

Application.—A direct cotton colour. Dyes unmordanted *cotton* brown from a neutral salt bath.

BENZO BROWN G (By.). An azo compound, containing four azo groups.

$$\begin{array}{l} \textit{Sulphanilic acid} \\ \textit{Metaphenylene} \\ \quad \textit{diamine} \\ \textit{Sulphanilic acid} \end{array} \left\{ \begin{array}{l} \textit{Metaphenylene diamine.} \\ \\ \textit{Metaphenylene diamine.} \end{array} \right.$$
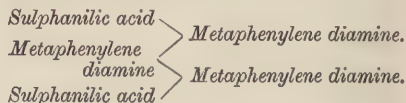
1887. Brownish-black powder, giving a reddish-brown solution in water; slightly

soluble in alcohol. In concentrated H_2SO_4, dull violet solution, brown ppt. on dilution.

Application.—As benzo brown B, but gives a yellower brown.

BENZO BROWN 5 R (By.) *v.* ALKALI BROWN (D.).

BENZO CHROME BLACK B (By.), N (By.), Mark B. Black powder. Aqueous solution, bluish-violet; slightly soluble in alcohol. Concentrated H_2SO_4, bright blue solution; on dilution, violet-blue.

Application.—Direct cotton dyes. Dyed in slightly alkaline bath, and subsequently saddened with $K_2Cr_2O_7$ and $CuSO_4$, producing very fast colours.

BENZO CHROME BLACK-BLUE B (By.). A similar product to the above.

BENZO CYANINE B (By.), 3 B (By.), R (By.). All bluish-grey powders. Mark B gives the following reactions:— Aqueous solution, violet - blue; alcoholic solution, blue. Concentrated H_2SO_4, greenish - blue solution; on dilution, becomes gradually violet-blue.

Application. — Direct cotton dyes, giving bright blue shades on *cotton.* Mark 3 B produces the greenest blue. May be saddened with metallic salts, but then yields duller shades. Employed also in *calico printing* for padding.

BENZO DARK BROWN (By.). Black powder. Aqueous solution, greenish-brown. Alcoholic solution, claret-red. Concentrated H_2SO_4, violet solution; on dilution, becomes darker, and then gives a greenish-brown ppt.

Application.—A direct cotton dye. Dyes blackish-brown shades on *cotton.*

BENZO DARK GREEN (B.), **G G** (By.). Direct cotton dyes, giving bluish and yellowish olives on unmordanted *cotton.*

BENZO FAST GREY (By.). Bluish-grey powder. Aqueous or alcoholic solutions, reddish-violet. Concentrated H_2SO_4, dull olive-green solution; on dilution, reddish-violet solution.

Application.—A direct cotton dye. Produces bluish - grey shades on *cotton* from a slightly alkaline bath.

BENZOFLAVIN (O.). An acridine derivative. *Hydrochloride of diamidophenyldimethyl acridine* (see ACRIDINE ORANGE). 1887. Brownish-yellow powder, giving a yellow solution in water. In alcohol, reddish-yellow solution, with greenish-yellow fluorescence. Concentrated H_2SO_4 gives a greenish-yellow solution, with strong green fluorescence; on dilution, orange ppt. is produced.

Application.—A basic colour. Dyes *wool, silk,* or tannin-mordanted *cotton* bright yellow.

BENZO GREY (By.). An azo compound, containing three azo groups.

Benzidine⟨ Salicylic acid.
　　　　 Alpha-naphthylamine.
Alpha-naphthol
　 sulphonic acid N W.

1890. Grey-black powder, giving a purplish-brown solution in water. In concentrated H_2SO_4, blue solution, which gives a black ppt. on dilution.

Application.—A direct cotton colour. Dyes unmordanted *cotton* grey from a neutral bath.

BENZO INDIGO-BLUE (By.). An azo compound.

Dianisidine⟨ Alpha-naphthylamine.
　　　　　 Dioxynaphthalene
　　　　　　 sulphonic acid.

1891. Grey powder, giving a dull blue solution in water. In concentrated H_2SO_4, dark greenish-blue solution; blue ppt. on dilution.

Application.—A direct cotton dye. Dyes unmordanted *cotton* dark blue from an alkaline bath.

BENZO NITROL. A name applied to *diazotised paranitraniline,* when applied as a developer for direct cotton dyes.

BENZO NITROL BLACK B, T (By.). 1899. Direct cotton dyes, specially suitable for developing with "Benzo nitrol."

BENZO OLIVE (By.). An azo compound, containing three azo groups.

Benzidine⟨ Salicylic acid.
　　　　 Alpha-naphthylamine.
Amidonaphthol
　 disulphonic acid R.

1891. Blackish powder, slightly soluble in water with a dark green colour. Insoluble in alcohol. In concentrated H_2SO_4, violet solution, giving a greenish-black ppt. on dilution.

Application.—A direct cotton colour. Dyes unmordanted *cotton* greenish-olive.

BENZO ORANGE R (By.) (Ber.) (L.). An azo compound, containing two azo groups.

Benzidine⟨ Salicylic acid.
　　　　 Naphthionic acid.

1887. Brown crystalline powder, giving an orange-yellow solution in water. In concentrated H_2SO_4, violet-blue solution; greyish-violet ppt. on dilution.

Application.—A direct cotton colour. Dyes unmordanted *cotton* orange from an alkaline bath.

BENZO PURPURIN B (By.) (Ber.) (L.) (Lev.). An azo compound.

Tolidine⟨ Beta-naphthylamine mono-
　　　　　 sulphonic acid Br.
　　　　 Beta-naphthylamine mono-
　　　　　 sulphonic acid Br.

5

1885. Brownish powder, giving a brownish-red solution in water. In concentrated H_2SO_4, blue solution; on dilution, dark-brown ppt.

Application.—A direct cotton colour. Dyes *cotton* red from an alkaline salt bath, *wool* red from a neutral bath.

BENZO PURPURIN 4 B (By.) (Ber.) (L.) (Lev.). Has also been sold under the names *Cotton red 4 B* (B.), *Imperial red*, *Eclipse red*, *Fast scarlet*, *Azamine 4 B*, &c., &c. An azo compound.

$$Toluidine \Big\langle {\text{Naphthionic acid.} \atop \text{Naphthionic acid.}}$$

1884. Brownish powder, giving brownish-red solution in water. In concentrated H_2SO_4, blue solution; blue ppt. on dilution.

Application.—As benzo purpurin B.

BENZO PURPURIN 6 B (By.) (Ber.) L.) (Lev.). An azo compound.

$$Tolidine \Big\langle {\text{Alpha-naphthylamine mono-} \atop \text{sulphonic acid } L. \atop \text{Alpha-naphthylamine mono-} \atop \text{sulphonic acid } L.}$$

1885. Red powder, giving orange-red solution in water. In concentrated H_2SO_4, blue solution; on dilution, blue ppt.

Application.—As benzo purpurin B.

BENZO PURPURIN 10 B (By.) (Ber.) (L.) (Lev.). An azo compound.

$$Dianisidine \Big\langle {\text{Naphthionic acid.} \atop \text{Naphthionic acid.}}$$

1885. Brownish-red powder, giving a carmine-red aqueous solution. In concentrated H_2SO_4, blue solution; on dilution, blue ppt.

Application.—As benzo purpurin B.

BENZO PURE BLUE (By.) *v.* DIAMINE SKY-BLUE (C.).

BENZOYL GREEN *v.* MALACHITE GREEN.

BENZYL VIOLET *v.* METHYL VIOLET 6 B.

BERBERINE *v.* BARBERRY BARK.

BERRIES *v.* PERSIAN BERRIES.

BETANAPHTHOL ORANGE *v.* ORANGE II.

BIARSENATE OF SODA *v.* SODIUM ARSENATE.

BICARBONATES OF AMMONIUM, POTASSIUM, and SODIUM *v.* the respective metals.

BICHROMATES OF AMMONIUM, POTASSIUM, and SODIUM *v.* the respective metals.

BIEBRICH ACID BLUE (K.). Greenish-blue powder. Aqueous or alcoholic solution, greenish-blue. Concentrated H_2SO_4, brownish-yellow solution; on dilution, becomes greenish-yellow, green, and finally greenish-blue.

Application.—An acid dye.

BIEBRICH BLACK A O, A N, 4 A N, 6 A N, 3 B O, 4 B N, R O (K.). *Mark 3 B O.* Violet-black powder. Aqueous solution, violet;

alcoholic solution, blue. Concentrated H_2SO_4, greenish-blue solution; on dilution, becomes dull blue, then violet.

Application.—Acid dyes, producing various shades of black on *wool* from a slightly acid bath; addition of $CuSO_4$ renders the colours faster to light.

BIEBRICH SCARLET *v.* PONCEAU 3 R B.

BILBERRY OR WHORTLEBERRY (*Vaccinium myrtillus*) contains a blue or purple dye, which dyes *wool* and *silk* without mordant.

BISMARCK BROWN. *Manchester brown, Phenylene brown, Vesuvine, Aniline brown, Gold brown, Leather brown, Cinnamon brown, English brown.* An azo compound. There are two distinct compounds, which are prepared from *metaphenylene diamine* and *metatoluylene diamine* respectively. The former was introduced in 1863, the latter in 1878. Phenylene compound—

$$Metaphenylene \atop diamine \Big\langle {\text{Metaphenylene diamine.} \atop \text{Metaphenylene diamine.}}$$

Black or red powders, giving red-brown solutions in water. In concentrated H_2SO_4, brown solutions, becoming redder on dilution.

Application.—Basic or direct cotton colours, which dye unmordanted *cotton* brownish-orange, tannin-mordanted *cotton* brown. *Wool* and *leather* brown from neutral or slightly acid bath.

BITTER ALMOND OIL GREEN *v.* MALACHITE GREEN.

BLACKS, "DIRECT" OR "ONE-DIP." These names, amongst others, are applied to those preparations containing logwood as dyestuff and iron as principal mordant, which are largely used for producing blacks by a single bath process. The possibility of using this method of dyeing depends upon two facts—firstly, that the iron-logwood colour-lake, though insoluble in water, dissolves unchanged in a dilute acid solution; and, secondly, that if wool is boiled in this feebly acid solution, it will withdraw and fix upon itself the colour-lake. That is to say, the attraction resulting from the affinity of the fibre for the colour-lake is able to overcome the tendency of the weak acid to keep the colour-lake in solution. If, however, the bath is strongly acid, its affinity for, or tendency to dissolve, the colour-lake is greater than that of the wool, and no dyeing takes place.

The dye-bath may be made up with the various ingredients (which usually consist of *logwood* or *logwood extract, ferrous sulphate, copper sulphate,* and *oxalic acid*), but the general practice is for dyers to buy the mixture ready prepared—"*Bonsor's black*" being a well-known compound of this type.

There are several methods of preparing these direct blacks, some of which are merely

mechanical mixtures of the necessary ingredients, whilst others consist of the iron and copper logwood lakes. Some also contain the oxalic acid necessary for their solution, but in most cases this has to be added by the dyer.

Reduced Black is of similar composition to the above, but the paste has been subjected to a reducing action.

BLACK LIQUOR *v.* IRON, PYROLIGNITE OF.
BLACK PASTE *v.* FAST BLACK (L.).
BLACKLEY BLUE *v.* SOLUBLE BLUE.
BLANC FIXE *v.* BARIUM SULPHATE.
BLAU (Ger.) = BLUE.
BLEACHING POWDER *v.* CALCIUM (CALCIUM CHLORO-HYPOCHLORITE).
BLEU (Fr.) = BLUE.
BLEU DE LYON *v.* SPIRIT BLUE.
BLEU DE NUIT *v.* SPIRIT BLUE.
BLEU DE PARIS *v.* SPIRIT BLUE.
BLEU FLUORESCENT *v.* FLUORESCENT BLUE.

BLUE BLACK B (B.). *Azo black O* (M.). An azo compound, closely allied to naphthol black.

$$Alpha\text{-}naph\text{-}thylamine \Big\langle \begin{array}{l} Beta\text{-}naphthylamine\ mono\text{-}\\ or\ disulphonic\ acid.\\ Beta\text{-}naphthol\ disulphonic\\ acid\ R. \end{array}$$

1882. Blue-black powder, giving blue-violet solution in water. In concentrated H_2SO_4, blue-green solution; on dilution blue solution, then blue ppt.

Application.—An acid colour. Dyes *wool* black from an acid solution.

BLUE BLACK R (B.). Very similar to blue black B, but prepared from a different sulphonic acid of beta-naphthylamine.

BLUE VITRIOL *v.* COPPER SULPHATE.
BOMBAY CATECHU *v.* CATECHU.
BONSOR'S BLACK *v.* BLACKS (DIRECT).
BORAX *v.* SODIUM BORATE.
BORDEAUX B (M.) (Ber.) (Lev.). *Bordeaux R extra* (M.), *Bordeaux B L* (C.), *Bordeaux G* (D.), *Fast red B* (B.), *Cerasine.* An azo compound.

Alpha-naphthylamine—Beta-naphthylamine trisulphonic acid R.

1878. Brown powder, giving magenta-red solution in water. In concentrated H_2SO_4, blue solution; on dilution, magenta-red.

Application.—An acid colour. Dyes *wool* and *silk* claret-red from an acid bath. Used also in preparing lakes.

BORDEAUX B X (By.). Two distinct azo compounds are sold under this name:

(1) *Amidoazo xylol — Beta-naphthol sulphonic acid S.*

1879. Brownish powder, giving brownish-red solution in water. In concentrated H_2SO_4, green solution; on dilution, brown-red ppt.

(2) *Amidoazo xylol — Beta-naphthol. disulphonic acid*

1879. Dark brown powder, giving red solution in water. In concentrated H_2SO_4, dark green solution; on dilution, first blue, then ppt. as brown-red flocks.

Application.—Acid dyes, both giving red shades on *wool* or *silk*.

BORDEAUX B L (C.) *v.* BORDEAUX B (M.).
BORDEAUX C O V (Ber.) *v.* BORDEAUX EXTRA (By.).
BORDEAUX D H (D. & H.) *v.* FAST RED D (B.).
BORDEAUX EXTRA (By.). *Bordeaux C O V* (Ber.), *Congo violet* (Ber.). An azo compound.

$$Benzidine \Big\langle \begin{array}{l} Beta\text{-}naphthol\ sulphonic\ acid\ B.\\ Beta\text{-}naphthol\ sulphonic\ acid\ B. \end{array}$$

1883. Brown powder, giving claret-red solution in water. In concentrated H_2SO_4, violet solution; violet ppt. on dilution.

Application.—A direct cotton colour. Dyes unmordanted *cotton* Bordeaux red from a salt bath; wool from an acid bath.

BORDEAUX G (D.) *v.* BORDEAUX B.
BORDEAUX G (By.). An azo compound.

Amidoazo toluol sul- — Beta-naphthol sulphonic acid   phonic acid S.

1879. Brown-red powder, giving a red solution in water. In concentrated H_2SO_4, dark blue; red ppt. on dilution.

Application.—An acid colour. Dyes *wool* and *silk* claret-red from an acid bath.

BORDEAUX R EXTRA (M.) *v.* BORDEAUX B.
BORDEAUX S (Ber.) *v.* FAST RED D (B.).
BRADFORD BLUE (Br.S. & Sp.). An obsolete rosaniline derivative. Basic dye.
BRAHMA ORANGE AND BRAHMA RED B, 2B, 6B (Z.). Azo compounds, derived from *benzidine.* Introduced 1889, now obsolete.

Application.—Direct cotton colours.

BRAZILEÏN *v.* REDWOODS (SOLUBLE).
BRAZILWOOD *v.* REDWOODS (SOLUBLE).
BRILLIANT ALIZARIN BLUE G PASTE (By.). Brownish-green paste. Aqueous and alcoholic solutions, greenish-blue. Concentrated H_2SO_4, olive-green solution; on dilution, violet.

Application.—A mordant dye. Gives dark bright blues on chrome-mordanted water. Used also in calico printing with acetate of chrome mordant.

BRILLIANT ALIZARIN BLUE R PASTE (By.) Violet paste. Aqueous solution, violet; alcoholic solution, reddish - violet. Concentrated H_2SO_4, olive-green solution; on dilution, bluish-green, then dull violet-blue.

Application.—As above, but gives somewhat redder shades.

BRILLIANT ALIZARIN CYANINE G PASTE (By.). Brownish-red paste. Aqueous solution, violet-blue ; alcoholic solution, blue. Concentrated H_2SO_4, yellowish-brown ; on dilution, reddish-violet.

Application.—A mordant dye, similar to the above.

BRILLIANT AZURIN B (Ber.). Greyish-black powder. Aqueous solution, bluish-violet ; alcoholic solution, violet. Concentrated H_2SO_4, greenish-blue ; on dilution, bluish-violet.

Application.—A direct cotton dye. Dyes unmordanted *cotton* blue.

BRILLIANT AZURIN 5G (By.) (Ber.) (L.). An azo compound, containing two azo groups.

$Dianisidine$ $\Big\langle$ $\begin{array}{l} Dioxynaphthalene\ mono\text{-} \\ \quad sulphonic\ acid. \\ Dioxynaphthalene\ mono\text{-} \\ \quad sulphonic\ acid. \end{array}$
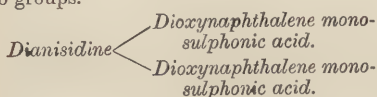
1889. Greyish-black powder, giving a bluish-violet solution in water. In concentrated H_2SO_4, greenish-blue solution ; on dilution, violet ppt.

Application.—A direct cotton colour. Dyes unmordanted *cotton* blue from a salt bath ; *wool*, blue from a neutral bath.

BRILLIANT BENZO GREEN B (By.). 1899. A direct cotton colour, giving bright bluish-green shades on unmordanted *cotton*.

BRILLIANT BLACK B (B.) *v.* NAPHTHOL BLACK 6 B.

BRILLIANT BORDEAUX S (Ber.). An acid red dye.

BRILLIANT CARMOISINE O (M.L. & B.) *v.* FAST RED C (B.).

BRILLIANT CHROME RED PASTE (By.). Crimson paste. Aqueous solution, red ; alcoholic solution, orange-red, with yellow fluorescence. Concentrated H_2SO_4, bluish-crimson ; on dilution, becomes slightly yellower.

Application.—A mordant dye. Used in *calico printing*, giving bright crimson shades.

BRILLIANT COCHINEAL 2 R AND 4 R (C.). Azo dyes allied to *palatine scarlet* (B.).

Application. — Acid colours. Dye *wool* and *silk* bright red from an acid bath.

BRILLIANT CONGO G (Ber.) (By.) (L.). An azo compound.
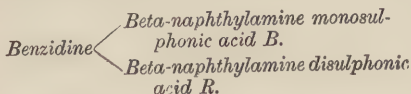
$Benzidine$ $\Big\langle$ $\begin{array}{l} Beta\text{-}naphthylamine\ monosul\text{-} \\ \quad phonic\ acid\ B. \\ Beta\text{-}naphthylamine\ disulphonic \\ \quad acid\ R. \end{array}$

1886. Brown powder, giving brownish-red solution in water. In concentrated H_2SO_4, blue solution ; on dilution, violet ppt.

Application.—A direct cotton colour. Dyes unmordanted *cotton* bright red from an alkaline bath.

BRILLIANT CONGO R (Ber.) (By.) (L.). The *tolidine* compound corresponding to the above. 1886. Brown powder, giving brownish-red solution in water. In concentrated H_2SO_4, blue solution ; on dilution, brownish-black ppt.

Application.—As *brilliant congo G.*

BRILLIANT COTTON BLUE GREENISH (By.) *v.* METHYL BLUE (C.).

BRILLIANT CRESYL BLUE 2 B (L.). A bright blue basic dye.

BRILLIANT CROCEINE M (C.). *Brilliant eroceïne* (By.), *Brilliant croceïne bluish* (C.), *Cotton scarlet* (B.), *Cotton scarlet 3 B* (K.), *Ponceau BO extra* (Ber.), *Paper scarlet blue shade* (M.). A secondary azo compound.

$Amidoazo\ benzol\ —\ Beta\text{-}naphthol\ disul\text{-} \\ \qquad\qquad\qquad\qquad phonic\ acid\ Y.$
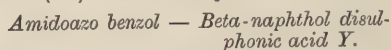
1882. Light brown powder, giving a cherry red solution in water. In concentrated H_2SO_4, red-violet solution ; on dilution, first blue, then brown ppt.

Application.—An acid colour. Dyes *wool* and *silk* in acid bath red. *Paper* and *cotton* on alum mordant a red, fast to light but not to washing. Used also as a lake, being precipitated by alumina hydrate and barium chloride.

BRILLIANT CROCEINE 3 B (By.). An acid dye, specially suitable for staining paper pulp.

BRILLIANT CROCEINE 3B (C.). Orange-red powder. Aqueous solution crimson. Alcoholic solution orange-red. Concentrated H_2SO_4, violet solution. On dilution, violet-brown ppt. becoming eventually violet.

Application.—An acid colour, giving bluish-scarlet shades.

BRILLIANT CROCEINE 9 B (C.). An azo compound.
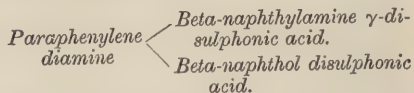
$\begin{array}{l} Paraphenylene \\ \quad diamine \end{array}$ $\Big\langle$ $\begin{array}{l} Beta\text{-}naphthylamine\ \gamma\text{-}di\text{-} \\ \quad sulphonic\ acid. \\ Beta\text{-}naphthol\ disulphonic \\ \quad acid. \end{array}$

1885. Brownish-red powder, soluble in water with a blue-red colour. In concentrated H_2SO_4, blue solution, becoming violet on dilution.

Application.—An acid colour. Dyes *wool* and *silk* bluish-scarlet from an acid bath.

BRILLIANT DIAZINE BLUE B AND 2 B (K.).

BRILLIANT GERANINE B AND 3 B (By.). Both are reddish-purple powders. Aqueous solution bluish-red, alcoholic solution redder. Concentrated H_2SO_4, blue solution, on dilution becomes gradually red.

Application. — Direct cotton dyes. Dye unmordanted *cotton* bright pinkish-red. Very suitable for padding.

BRILLIANT GREEN (B.) (By.) (C.) (M.) (D. & H.) (L.) (K.) (O.). *Malachite green G* (B.), *Diamond green G* (B.), *Ethyl green* (Ber.), *Emerald green* (By.), *Fast or Solid green J* (Mo.) (P.), *Solid green T T O* (S. C. I.). A triphenylcarbinol derivative. *Sulphate or zinc chloride double salt of tetra-ethyldiamidotriphenyl carbinol.* 1879. Golden crystals (sulphate), giving a green solution in water or alcohol. In concentrated H_2SO_4, yellow solution. On dilution, first dark yellow, then yellowish-green, and finally green.

Application.—A basic colour. Dyes *wool, silk, jute, leather,* or tannin and tartar emetic mordanted *cotton,* green ; gives yellower shade than malachite green.

BRILLIANT HESSIAN PURPLE (L.) (Ber.) (By.). An azo compound.

$$Diamidostilbene\ disulphonic\ acid \Big\langle \begin{array}{l} Beta\text{-}naphthylamine\ mono\text{-}\\ sulphonic\ acid\ B.\\ Beta\text{-}naphthylamine\ mono\text{-}\\ sulphonic\ acid\ B. \end{array}$$

1886. Dark red powder, giving a purple-red solution in water. In concentrated H_2SO_4, blue solution ; on dilution, blue-black ppt.

Application.—A direct cotton colour. Dyes unmordanted *cotton* bluish-red.

BRILLIANT ORANGE G (M.) *v.* Croceïne Orange.

BRILLIANT ORANGE G (Ber.). Brownish-red powder. Aqueous or alcoholic solution brownish-red. Concentrated H_2SO_4, purple solution ; on dilution, brown precipitate.

Application.—A direct cotton dye. Dyes unmordanted *cotton* bright orange.

BRILLIANT ORANGE O (M.) *v.* Orange GT (By.).

BRILLIANT ORANGE R (M.). *Scarlet G R* (Ber.), *Scarlet R* (By.), *Orange N* (K.), *Xylidine orange.* An azo compound.

Xylidine — Beta-naphthol sulphonic acid S.

1879. Cinnabar red powder, giving a yellowish-red solution in water. In concentrated H_2SO_4, cherry-red solution ; on dilution, reddish-brown ppt.

Application.—An acid colour. Dyes *wool* and *silk* yellow-red from an acid bath.

BRILLIANT ORCHIL C (C.). An azo compound. 1893.

Application.—An acid colour. Dyes *wool* and *silk* very level orchil-red shades.

BRILLIANT PONCEAU G (C.) *v.* Ponceau 2 R (Ber.).

BRILLIANT PONCEAU G G (C.) *v.* Ponceau 2 G (Ber.).

BRILLIANT PONCEAU 4 R (By.) *v.* Double Brilliant Scarlet Extra S (Ber.).

BRILLIANT PONCEAU 4 R (C.) (By.) (D.) *v.* Cochineal Red A (B.).

BRILLIANT PURPURIN 5 B (Ber.) (By.) (L.). An azo compound.

$$Tolidine \Big\langle \begin{array}{l} Alpha\text{-}naphthylamine\ sulphonic\\ acid\ L.\\ Beta\text{-}naphthylamine\ sulphonic\\ acid\ Ber. \end{array}$$

Application. — A direct dyeing cotton colour. Dyes unmordanted *cotton* bright red from an alkaline bath.

BRILLIANT PURPURIN R (Ber.) (By.) (L.). An azo compound.

$$Tolidine \Big\langle \begin{array}{l} Beta\text{-}naphthylamine\ disul\text{-}\\ phonic\ acid\ R.\\ Naphthionic\ acid. \end{array}$$

Red powder, giving a red solution in water. In concentrated H_2SO_4, blue solution ; on dilution, blue-black ppt.

Application.—*v.* Brilliant Purpurin 5 B.

BRILLIANT RED (Sch.) *v.* Fast Red A (B.).

BRILLIANT SCARLET (Lev.) *v.* Cochineal Red A (B.).

BRILLIANT SULPHONAZURIN R (By.). Dull violet-blue powder. Aqueous solution, dull blue. Alcohol (easily soluble) reddishblue solution. Concentrated H_2SO_4, bluishred solution. On dilution, purplish-red precipitate.

Application.—A direct cotton dye. Dyes unmordanted *cotton* bright blue.

BRILLIANT YELLOW (Sch.) *v.* Naphthol Yellow R S (By.). A nitro compound. *Sodium salt of dinitro alphanaphthol alpha-monosulphonic acid.* 1884. Golden-yellow powder, soluble in water. On heating, the dry powder swells up and deflagrates. In concentrated H_2SO_4 it gives a pale yellow solution.

Application.—An acid colour. Dyes *wool* and *silk* yellow from an acid bath.

BRILLIANT YELLOW (L.) (Ber.) (By.). An azo compound.

$$Diamido\ stilbene\ disulphonic\ acid \Big\langle \begin{array}{l} Phenol.\\ Phenol. \end{array}$$

1886. Light brown powder, giving reddishyellow solution in water. In concentrated H_2SO_4, violet solution ; on dilution, violet ppt.

Application.—A direct cotton colour. Dyes unmordanted *cotton* yellow from an alkaline bath. Is very sensitive to acids.

BRILLIANT YELLOW S (B.). *Brilliant yellow* (M.), *Yellow W R* (S.C.I.), *Curcumin* (G.). An azo compound.

Sulphanilic acid—Diphenylamine sulphonic acid.

Orange-yellow powder, giving a yellow solution in water. In concentrated H_2SO_4, bluered solution ; on dilution, magenta-red.

Application.—An acid colour. Dyes *wool* or *silk* yellow from an acid bath.

BRITISH GUM *v.* Thickeners.

BROWN NP and NPS (D. & H.).   An azo compound.

Paranitraniline — Pyrogallol.

1891.   Brown paste.

Application.—Dyes *wool* mordanted with chrome a brown fast to milling.

BUCKWHEAT (*Polygonum fagopyrum*) has been investigated by Schunck, and appears to contain a yellow dye allied to *Maclurin* (old fustic).

BUFFALO RUBINE (Sch.) *v.* Azo Bordeaux (By.).

BUTTER YELLOW.   An azo compound.

Aniline — Dimethylaniline.

1874.   Yellow plates, melting at 115° C.   Insoluble in water.   In concentrated H_2SO_4, yellow solution, becoming red on dilution. In oils, soluble.

Application.—Used for colouring *butter, oils,* &c.

C

CABBAGE RED.   *Red cabbage* contains a considerable amount of colouring matter, to which the name *cauline* has been given.   It is probably identical with *cyanine*, and is largely used in colouring spurious wines.

CACHOU DE LAVAL (P.).   Obtained by fusing vegetable substances, such as *sawdust, bran,* or *starch ;* or animal products, such as *blood, horn,* or *feathers,,* with alkaline sulphides.   Probably a polymer of the base,

$$\begin{matrix} H - S - C = C \\ | \quad\quad | \\ H - S - C = C \end{matrix} \Big\rangle S$$
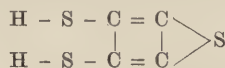
(Richardson & Akroyd).   1873.   The commercial article is very impure, containing only 20 to 30 per cent. colouring matter.   It is usually prepared from sawdust, but in addition to the bodies above mentioned it may be obtained from *saccharose, gallic acid, succinic acid,* or *furfurane* by fusing with Na_2S.

Sold as porous hygroscopic black lumps. Aqueous solution is greenish-black, but becomes brown on standing, with precipitate of colouring matter and sulphur.   Addition of H_2SO_4 to the aqueous solution causes evolution of H_2S and precipitation of dye. Concentrated H_2SO_4, olive solution evolving H_2S.

According to Richardson & Akroyd, [*] a characteristic test for cachou is as follows :—Dissolve the colour in baryta water and pass CO_2.   A blood-red colour is produced, which is not destroyed by boiling or evaporation to dryness.

Application.—Requires a special process. Applicable only to vegetable fibres.   The dye

[*] *Journ. Soc. Chem. Ind.,* May, 1898.

is dissolved in hot water, sodium chloride, sulphate or bisulphate is added, and the material is dyed for about an hour.   It is then washed, and the colour fixed by means of one of the following solutions :—

		Grms. per litre.
1. Sulphuric acid,	. . .	20
2. Hydrochloric acid,	. .	50
3. Bichromate of potash, .	.	2 to 3
4. Copper sulphate,	. . .	5
5. Ferric sulphate, 4° Tw.		

The fixing bath is used warm.

The colour obtained is influenced to some extent, but not greatly, by the nature of the fixing agent employed ; the *mineral acids* produce the yellowest colours, *bichromate* slightly more neutral colours, *copper sulphate* greyer colours.   All are very fast to washing and soaping, and fairly fast to light.

Cachou dyes serve as mordants for basic dyes, and when fixed with metallic salts also for mordant dyes.

CACTUS.—The flowers of many species of *Cactus*, particularly *C. speciosus*, appear to contain a colouring matter identical with that of cochineal, and this is interesting, as tending to show that this important colouring matter is really of vegetable and not of animal origin, and is merely extracted from the plant by the insect.

CAKE ALUM *v.* Aluminium Sulphate.

CALCIUM, Ca = 40.   The metal occurs in nature in large quantities, combined with carbonic, sulphuric, and phosphoric acids.

It can be prepared by heating calcium iodide with sodium in covered iron crucibles. It has a yellow colour, and decomposes water. Metallic calcium is of no importance commercially at the present time.

CALCIUM ACETATE, *Acetate of lime,* $Ca(C_2H_3O_2)_2$.

Preparation.—*Brown* or *grey acetate of lime* is prepared from pyroligneous acid by neutralisation with lime.   After standing, the liquid is syphoned off and evaporated, the tarry impurities which rise to the surface being skimmed off.   After removal from the evaporating vessel, the crude acetate is carefully dried.   It decomposes when strongly heated. The acetate of calcium may be purified by redissolving in water, filtering, and crystallising. Crystals of the composition $Ca(C_2H_3O_2)_2 + 2H_2O$ are formed ; they are easily soluble in water, the solution being acid to litmus.

White acetate of lime is prepared by neutralising about 7 parts of 30 per cent. acetic acid with 1 part of quicklime (calcium oxide).

Application.—Calcium acetate is used as a mordant, calcium forming an essential part of the alizarin lakes   Acetic acid and many other acetates are prepared from this salt.

Properties.—The commercial article generally contains about 65 per cent. of the pure

substance, and 1 to 8 per cent. of matter insoluble in water.

Calcium sulphate, hydrate, and carbonate, together with more or less tarry matter, are the usual impurities.

Analysis — Estimation of Acetic Acid in Calcium Acetate and other Acetates. — The amount of acetic acid present is determined by distillation with phosphoric acid, as recommended by Stillwell and Gladding, and described in *Allen's Commercial Organic Analysis*, vol. i., p. 479. A retort of 100 c.c. capacity, the tube of which should have been previously bent downward about 4 inches from the end, is employed. The extremity of the retort is connected with a small Liebig's condenser, the inner tube of which at its lower end passes downwards into a flask containing water or 50 c.c. $\frac{N}{2}$ caustic soda and a drop of phenolphthaleïn.

The receiver consists of a wide-mouthed flask of 1 litre capacity, fitted with a rubber stopper having two holes, through the smaller of which passes the narrow end of a small tube (such as is used for drying purposes) filled with glass beads. The water or standard soda used should be poured down this tube, the retort tubulus being meanwhile left open. The receiving flask should be placed in a vessel of cold water and kept cool during the distillation.

One grm. of the sample is worked through a wide short-necked funnel into the retort with 15 c.c. of water. The retort is fitted with a tapped funnel, through which is poured a solution of 5 grms. of glacial acetic acid in 10 c.c. of water. During the operation the neck of the retort is inclined slightly upwards to prevent any liquid being carried over mechanically.

The retort, which is placed on wire gauze, is gently heated, and the liquid distilled until it is reduced to a volume of not more than 10 c.c., when 25 c.c. of water are introduced through the funnel, and the distillation continued until the volume of the liquid is again reduced to 10 c.c. The addition of water and distillation to small bulk are repeated three more times, when the whole of the acetic acid will have passed over. The distillate, after rinsing the condenser into the receiver, is titrated with $\frac{N}{2}$ sulphuric acid; or in the event of water only having been placed in the receiver, $\frac{N}{2}$ caustic soda should be used.

The phosphoric acid used must be free from nitric acid. If the sample or the phosphoric acid contain chlorides, a little silver sulphate must be added to the contents of the retort to prevent hydrochloric acid distilling over.

Example.—0·9864 grm. sample distilled into 50 c.c. $\frac{N}{2}$ NaOH required 28·77 c.c. $\frac{N}{2}$ H$_2$SO$_4$ to discharge the pink colour of the indicator (phenolphthaleïn).

50 − 28·77 = 21·23 c.c. $\frac{N}{2}$ NaOH required for the sample.

1 c.c. $\frac{N}{2}$ NaOH = 0·03 grm. C$_2$H$_4$O$_2$ or 0·0395 grm. Ca(C$_2$H$_3$O$_2$)$_2$.

∴ $21·23 \times 0·03 \times \dfrac{100}{0·9864} = 64·55$ per cent. acetic acid (C$_2$H$_4$O$_2$).

Pure calcium acetate yields 74·68 per cent. acetic acid; or

$21·23 \times 0·0395 \times \dfrac{100}{0·9864} = 85·0$ per cent. calcium acetate.

CALCIUM CARBONATE, CaCO$_3$. *Limestone, Chalk.* Carbonate of lime is widely distributed in nature, forming the bulk of many mountain ranges. It often occurs in conjunction with magnesium carbonate as *dolomite. Marble, limestone,* and *coral* are also forms of calcium carbonate. It may be obtained in a pure state by treating calcium chloride solution with an alkaline carbonate, preferably ammonium carbonate. It is a white powder, almost insoluble in pure water (1 litre dissolves 0·18 grm. CaCO$_3$), but it dissolves in water containing carbon dioxide. The chalk is thrown out of solution, however, on expelling the gas by boiling the liquid. The presence of chalk in natural waters from the above cause produces what is termed *temporary hardness.*

Calcium carbonate dissolves in acids with effervescence. It is used as a mild alkali for the neutralisation of acid liquids, and as an addition to the dye-bath in the dyeing of alizarin, and in certain cases for fixing mordants. A light, soft, *precipitated chalk,* free from sodium carbonate or hydrate, and almost completely soluble in acetic acid, is best for these purposes.

An aqueous extract of chalk will turn red on the addition of phenolphthaleïn if carbonates or hydrates of the alkalies are present.

CALCIUM CHLORIDE, CaCl$_2$, is prepared by dissolving lime or chalk in hydrochloric acid. On the large scale, it is obtained as a by-product in the manufacture of ammonia—soda, &c. Chloride of calcium is very deliquescent, and very easily soluble in water. It is found in commerce as a white, solid, dense or porous mass. It crystallises from concentrated solutions as CaCl$_2$ + 6H$_2$O. Anhydrous calcium chloride is used as a drying agent in the laboratory.

CALCIUM CHLORO-HYPOCHLORITE, CaOCl$_2$. *Bleaching powder, Chloride of lime.*

Preparation.—Chlorine, on passing over thin layers of calcium hydrate, is absorbed,

forming this most important substance, bleaching powder. The chlorine for this purpose is obtained by various methods. (1) By treating manganese dioxide with hydrochloric acid. (2) By Mond's process, which consists in volatilising ammonium chloride, and decomposing the vapours by means of hot magnesia in small lumps. The chlorine is completely retained by the magnesia, and on passing air through the oxychloride, magnesia is reproduced and chlorine is expelled. (3) By an electrolytic process, in which potassium or sodium chloride is used as the electrolyte, and mercury is employed alternately as anode and cathode. In this process, chlorine is liberated and an amalgam of potassium or sodium is formed, which in contact with water is decomposed, potash or soda being produced, and mercury set free. The exact constitution of bleaching powder and the chemistry of its production have not yet been elucidated. It is probable that it consists for the greater part of calcium chloro-hypochlorite, $Ca{<}^{Cl}_{OCl}$, as it is not possible to extract the calcium chloride by means of alcohol, although, according to the generally accepted equation representing the action of chlorine on slaked lime, calcium chloride and calcium hypochlorite are formed—

$$2Ca(OH)_2 + 2Cl_2 = Ca(OCl)_2 + CaCl_2 + 2H_2O.$$
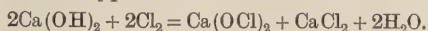
Carbon dioxide is capable of expelling almost the whole of the chlorine.

Properties.—Commercial *chloride of lime* generally contains 35 to 37 per cent. available chlorine. By the term "available" is understood the chlorine which is capable of being evolved in the free state on the addition of an acid. It is a white powder, having a smell resembling that of chlorine. On exposure to the air, moisture and carbon dioxide are slowly absorbed and chlorine gradually evolved. Bleaching powder, even when stored in closed vessels, decomposes slowly, but light accelerates the decomposition.

It is soluble in about twenty times its weight of water, the alkaline solution having strong bleaching properties. On boiling, the aqueous solution evolves oxygen and forms calcium chloride and chlorate. The carbon dioxide of the atmosphere gradually decomposes solutions of bleaching powder in water, hypochlorous acid and eventually free oxygen being produced :

(1) $2CaOCl_2 + H_2CO_3 = CaCO_3 + CaCl_2 + 2HOCl$
(2) $HOCl = HCl + O.$
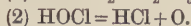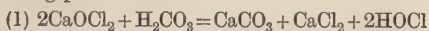
The bleaching action of bleaching powder is due to the oxygen which it liberates, as shown by the above equation. The addition of acids to the liquid causes the decomposition to take place more quickly, a comparatively small amount of acid being sufficient to destroy the equilibrium of the chlorine compound, and gradually cause its complete dissociation. G. Lunge has patented a method in which formic or acetic acid is used for the above purpose. A minute quantity of a salt of cobalt placed in a boiling solution of bleaching powder causes steady evolution of oxygen.

Uses.—Bleaching powder is employed in the bleaching of cotton, hemp, flax, and materials required in the manufacture of paper, also as a disinfectant, and as a discharge in calico printing.

Bleaching powder is used in the form of a clear solution obtained by digesting the "bleach" in cold water, and decanting the supernatant liquid after standing to deposit insoluble matter. The solution containing about 7 per cent. available chlorine is a market article.

Other bleaching solutions (the active constituents of which are hypochlorites) are used —for instance, *Eau de Javelle* and *Eau de Labarraque*. *Magnesium*, *zinc*, and *aluminium* hypochlorite (*Wilson's bleaching liquor*) are sometimes employed.

Analysis of Bleaching Powder.—Besides the chief constituents of bleaching powder ($CaOCl_2$), other compounds are present in greater or less quantity — viz., *calcium hydrate*, *calcium chloride*, and *calcium chlorate*. If sufficient care has not been exercised in the manufacture, calcium chlorate may exist to the extent of 10 per cent. The value of chloride of lime for bleaching purposes depends solely upon the amount of *available chlorine* present. Chlorate of calcium is of no value as a bleaching agent.

Penot's method of analysis is based upon the conversion of an *alkaline arsenite* into an *arsenate* when a solution of the former is added to a hypochlorite.

$$Na_3AsO_3 + O = Na_3AsO_4.$$

When sufficient of the sodium arsenite has been added to the bleaching powder solution the latter gives no further reaction for free chlorine.

Preparation of Deci-normal Sodium Arsenite Solution.—4·95 grms. of pure re-sublimed arsenious oxide and 10 grms. of pure sodium bicarbonate are dissolved in about 250 c.c. of water. The arsenious oxide must be in fine powder, and is best added to the hot solution of sodium bicarbonate, and the mixture heated to boiling to promote solution. When quite clear, it is cooled and diluted to 1 litre. 1 c.c. of sodium arsenite solution = ·00355 grm. Cl.

In order to check this solution about ½ grm. of iodine is ground with 0·1 grm. potassium iodide and the mixture heated gently in a

porcelain crucible covered with a watch-glass, which, together with another watch-glass and clip, has been previously weighed. The crucible and contents should be heated for a short time to drive off any moisture before the watch-glass is placed over it. When sufficient iodine has condensed the watch-glass is removed, covered with the remaining tared one, and placed in the clip until cold, when the whole is weighed. The glasses are placed in 20 c.c. of 10 per cent. potassium iodide solution in a beaker, and as soon as all is dissolved, sodium arsenite is added from a burette until the solution is light yellow ; starch solution is then added, and the titration continued until the blue colour disappears. The number of c.c. of arsenite required mul- tiplied by 0·0127 should be exactly the weight of iodine used.

Preparation and Titration of Bleaching Powder Solution. — The sample is spread out on a sheet of paper and all lumps are crushed, and the whole quickly mixed with the aid of a strong spatula. 7·10 grms. are weighed on a watch-glass and transferred to a small mortar, in which the substance is rubbed into a thin cream with water. After allowing the coarser particles to subside, the turbid liquid is poured through a funnel into a litre flask, and the residue in the mortar again ground up with more water. This is repeated three or four times, when the whole of the solid will have been transferred to the flask. After thoroughly washing the pestle and mortar, the liquid in the flask is made up to 1 litre and the solution well agitated. 50 c.c. (0·355 grm.) of the turbid liquid are withdrawn immediately after shaking the flask by means of a pipette and titrated in a porcelain basin with continual stirring with $\frac{N}{10}$ arsenite solution, until the liquid ceases to give a blue or violet colour, when a drop is placed with a glass rod on a filter paper moistened with a solution of potassium iodide and starch. This paper may be readily prepared by saturating filter paper with a solu- tion made by boiling about $\frac{1}{4}$ grm. of potato starch, $\frac{1}{4}$ grm. of potassium iodide, and $\frac{1}{10}$ grm. of sodium carbonate, with 50 c.c. of water. Each c.c. of the arsenite solution indicates 1 per cent. available chlorine. If 34 c.c. arsenite solution were required, 34 per cent. of available chlorine is present. If any other weight of bleaching powder, or a bleaching solution, had been used, for example, 40 grms. of solution, and after diluting to a litre, 50 c.c. (2 grms. solution) required 45 c.c. of arsenite solution.

1 c.c. $\frac{N}{10}$ sodium arsenite = 0·00355 grm. Cl.

∴ $\frac{0·00355 \times 45 \times 100}{2}$ = 7·98 per cent. of avail-
able chlorine.

Bunsen's method depends upon the oxida-

tion of sodium thiosulphate. It records the amount of chlorine present as chlorate as well as hypochlorite ; consequently it is not so well adapted for the valuation of bleaching powder as Penot's method. If both methods are used, the difference between the two results shows the amount of chlorine present as chlorate.

Preparation of Deci-normal Sodium Thio- sulphate Solution.—24·8 grms. of pure crystal- lised sodium thiosulphate, $Na_2S_2O_3$, $5H_2O$, are dissolved in 1 litre of water. The resulting solution may be standardised either by $\frac{N}{10}$ iodine solution, or, preferably, by a deci-normal solution of potassium bichromate, containing exactly 4·917 grms. of pure $K_2Cr_2O_7$ in a litre. 25 c.c. of $\frac{N}{10}$ $K_2Cr_2O_7$ solution are run from a burette into a stoppered bottle of about 500 c.c. capacity, 10 c.c. of a 10 per cent. solution of potassium iodide, 200 c.c. of water, and 5 c.c. of con- centrated hydrochloric acid are added. The thiosulphate solution is then gradually added from a burette until the solution is nearly colourless, a rotary motion being imparted to the solution meanwhile. A little starch solution is then added, and the titration con- tinued until the blue colour just disappears.

The starch solution is prepared by rubbing $\frac{1}{2}$ grm. of pure potato starch into a cream with a little water in a mortar and pouring it into 250 c.c. of boiling water, boiling for 15 minutes, cooling, and pouring off the clear solution. It is best freshly prepared. If the thiosulphate solution be strictly normal 25 c.c. of it will be required. 1 c.c. of $\frac{N}{10}$ thiosul- phate = 0·00355 grm. Cl. In this reaction the bichromate liberates an equivalent amount of iodine from the excess of potassium iodide used.

Titration of Bleaching Powder.—25 c.c. of the bleaching powder solution prepared as above described (0·1775 grm.) are withdrawn and diluted with 200 c.c. of water and 10 c.c. of potassium iodide solution, and 5 c.c. concentrated hydrochloric acid added. The liquid is then titrated with $\frac{N}{10}$ thiosulphate in exactly the same manner as in standard- ising with bichromate.

Example.—25 c.c. (0·1775 grm.) of the solution made as above described required 18·5 c.c. hyposulphite solution, and 25 c.c. tested by Penot's method required 17 c.c. $\frac{N}{10}$ sodium arsenite solution.

18·5 − 17·0 = 1·5.
∴ 1·5 × 2 (= 0·355 grm. solution)
    = 3 per cent. chlorine as chlorate.

If the per cent. of available chlorine be accepted from the latter method, the amount found—viz., 18·5 × 2 = 37 per cent.—will include the chlorine as chlorate.

Lunge* has devised a gasometric method depending upon the evolution of oxygen when a solution of bleaching powder or hypochlorite is mixed with peroxide of hydrogen. *Bleaching liquors and other hypochlorites* may be analysed in exactly the same manner as chloride of lime.

CALCIUM HYDROXIDE, Ca(OH)$_2$ (*Calcium hydrate, Slaked lime*). Calcium hydroxide is formed by the action of water on calcium oxide, CaO + H$_2$O = Ca(OH)$_2$; or, as it is commonly called, by "slaking" lime, which is best effected by first moistening the quicklime with small quantities of hot water until the mass becomes very hot and begins to break up, and then adding cold water. If the raw material contained clay, or has been heated too strongly, the quicklime does not slake well, and yields no good caustic lime. Calcium hydroxide forms a white powder of 2·01 specific gravity, which dissolves in 730 parts of water at 15°, and is less soluble at higher temperatures. This solution is called *lime-water*. Water containing calcium bicarbonate or organic substances is not well suited for making lime-water, as the lime will soon be covered with insoluble substances, and will be but slowly dissolved by the water. Lime-water containing undissolved slaked lime, so as to appear milky, is known as *milk of lime.*

Calcium hydroxide is decomposed at a red heat into calcium oxide and water. It is a strong diacid base. Its solutions turn red litmus blue, and absorb carbon dioxide from the air with avidity, forming insoluble calcium carbonate which renders the liquid turbid. By bleachers and dyers it is used as a cheap alkali for bleaching cotton, and as a fixing agent for iron mordants, in the preparation of the indigo vat, &c. When solid (*i.e.,* lumpy) lime has been long in contact with cotton, it is liable to tender the fibre and to cause uneven dyeing.

Analysis of Lime.—In the preparation of caustic lye it is often necessary to test the quicklime used and the residue or "lime-mud" remaining in the causticising pans. The following methods are taken from Lunge and Hurter's Alkali Makers' Pocket-Book :—

I. QUICKLIME—(*a*) *Free Lime* (CaO).—An average sample both of lumps and smaller pieces is carefully taken, broken up, and pulverised ; 100 grms. are taken and completely slaked, and the "milk" is placed in a half-litre flask ; the flask is filled up to the mark and well shaken, when 100 c.c. are transferred to a half-litre flask, which is filled up and the whole well mixed ; 25 c.c. of the contents are then taken for the test (equal to 1 grm. of quicklime), and titrated with normal oxalic acid, using litmus or phenolphthaleïn as indicator. The colour is changed

* *Journ. Soc. Chem. Ind.,* 1890, p. 22.

when all free lime has been saturated and before the calcium carbonate is attacked.

(*b*) *Carbon Dioxide* (CO$_2$).—Titrate free lime and calcium carbonate together by dissolving in an excess of standard hydrochloric acid and titrating back with standard alkali. By deducting the lime estimated as in (*a*), the quantity of calcium carbonate is obtained.

II. SLAKED LIME — (*a*) *Water.* — Weigh about 1 grm. from a stoppered glass tube, and heat it gradually in a platinum crucible, finally to a strong red heat. Allow to cool in the desiccator, and weigh. The loss of weight is equal to H$_2$O + CO$_2$.

(*b*) *Carbon dioxide* is estimated as in quicklime.

III. LIME-MUD—(*a*) *Sodium Carbonate and Hydrate.*—Evaporate to dryness with addition of ammonium carbonate (in order to decompose the insoluble sodium calcium carbonates), repeat this, digest with hot water, filter, wash, and test the filtrate for alkali. The soda may have been originally present as sodium hydrate or as sodium carbonate. It is expressed in terms of Na$_2$O (0·031 grm. per c.c. of $\frac{N}{1}$ acid).

(*b*) *Caustic Lime.*—Titrate with oxalic acid as described under quicklime. This indicates sodium hydrate as well, for which half the result of test (*a*) may be assumed without any serious error.

(*c*) *Calcium Carbonate.* — Titrate with $\frac{N}{1}$ hydrochloric acid and methyl orange, and deduct from the volume required the number of c.c. required in tests (*a*) and (*b*).

TABLE SHOWING AMOUNT OF LIME IN MILK
OF LIME.
(*Calculated from Blattner.*)

Degrees Twaddell.	Grms. CaO per litre.	Lbs. CaO per cubic foot.
2	11·7	0·7
4	24·4	1·5
6	37·1	2·3
8	49·8	3·1
10	62·5	3·9
12	75·2	4·7
14	87·9	5·5
16	100	6·3
18	113	7·1
20	126	7·9
22	138	8·7
24	152	9·5
26	164	10·3
28	177	11·1
30	190	11·9
32	203	12·7
34	216	13·5
36	229	14·3
38	242	15 1
40	255	15·9
42	268	16·7
44	281	17·6
46	294	18·4
48	307	19·2
50	321	20·0

CALCIUM LIGNOSULPHONATE. *Lignorosin.* A by-product obtained in one of the processes of manufacturing paper pulp from lignocellulose fibres.

It is a dark brown syrup, used as an assistant in mordanting wool with chrome.

Wool mordanted in this manner has a pale brown colour, hence it is unsuitable for many pale shades.

This substance is much cheaper than lactic acid.

A. Raaz * considers that it will replace lactic acid to some extent in wool dyeing.

Seidel and Hanak † have used this sulphite liquor in the indigo vat. Lignorosin contains about 50 per cent. of solid matter (calcium lignin sulphonate), 6·2 per cent. of ash, 4 per cent. of organic sulphur, and traces of sulphurous acid. When used as an assistant enough sulphuric acid should be added to neutralise the calcium of the lignorosin and the potassium of the bichromate.

CALCIUM OXIDE, CaO (*Quicklime, Burnt Lime*). Calcium oxide is prepared by subjecting calcium carbonate (*marble, limestone, oyster shells,* &c.), to a bright red heat, $CaCO_3 = CaO + CO_2$. The purest product is obtained from marble. Calcium oxide is a white, amorphous, porous mass which cannot be melted. Its specific gravity is 3·08. It attracts moisture with great avidity, and with evolution of heat. It also absorbs carbonic acid from the air.

CALCIUM SULPHATE, $CaSO_4$.—Calcium sulphate is usually present in solution in natural waters, and is the chief substance which gives rise to the *permanent hardness of water.* It occurs in the crystalline form as the mineral *anhydrite,* $CaSO_4$, and combined with water as *gypsum* and *alabaster,* $CaSO_4 + 2H_2O$. Gypsum, when moderately heated, loses its water, forming the so-called *plaster of Paris.* This takes up 2 molecules of water when moistened again, and forms a solid mass. Artificially prepared calcium sulphate or "*annaline*" is used by paper manufacturers.

CALCIUM SULPHOCYANIDE or THIO-CYANATE, $Ca(CNS)_2$, crystallises with three equivalents of water, and is very soluble in water. The crude liquor obtained from the hydraulic mains of gas works is utilised for the preparation of other sulphocyanides used in textile printing.

CALIATUR (*Cariatur*) v. REDWOODS (INSOLUBLE).

CALORIFIC POWER v. COAL.

CALORIMETER v. COAL.

CAMPANULIN (Ber.) v. MUSCARIN (D. & H.).

CAMPEACHY WOOD v. LOGWOOD.

CAMWOOD v. REDWOODS (INSOLUBLE).

* *Journ. Soc. Chem. Ind.,* 1898, p. 923.
† *Ibid.,* 1898, p. 844.

CANAIGRE. Although this tannin has been known and used in Mexico for a long time, it has only recently been introduced here as a commercial article. It is obtained from the tuberous root of *Rumex hymenosepalus,* and thus belongs to the same family as the common dock (*Rumex crispus*), which it somewhat resembles in appearance. The plant grows to a height of from 1 to 3 feet, and the tubers are 6 to 10 inches long, and 1½ to 2 inches in diameter. When freshly dug up they are comparatively soft, and yellow to red in colour; but on drying become hard and nearly black. Canaigre is now extensively cultivated in Texas, New Mexico, and Arizona, and South-Western United States generally, and exported in large quantities to Europe. It contains 25 to 35 per cent. of tannin, the nature of which has not been determined.

CANARIN (*Persulphocyanogen yellow*). An oxidation product of sulphocyanic acid, probably

$$HS(CN)_2 \begin{cases} S \\ | \\ S \end{cases}$$
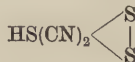
1883. Orange-yellow powder, insoluble in water, alcohol, or ether. Soluble in NaOH or borax solution. In concentrated H_2SO_4, yellow solution, precipitated on dilution.

Application.—Used as a yellow pigment in *calico printing,* &c.

CANELLE, old name for *Bismarck brown.*

CAPILLARY ANALYSIS v. COAL-TAR COLOURS.

CAPRI BLUE G and N (L.) (By.). An oxazine derivative. *Dimethylphenyl ammonium dimethylamidotolyloxazine zinc chloride double salt.* 1890. Green crystals, giving a blue solution in water or alcohol. In concentrated H_2SO_4, green solution, becoming red on dilution.

Application.—A basic colour. Dyes *cotton* mordanted with tannin, and tartar emetic greenish-blue.

CAPRI GREEN B, G and G G (L.).

CARBAMATE OF AMMONIA v. AMMONIUM CARBAMATE.

CARBAMIC ACID v. AMMONIUM CARBAMATE.

CARBAZOL v. ANTHRACENE.

CARBAZOL YELLOW (B.). An azo compound.

$$Diamidocarbazol \begin{cases} Salicylic\ acid. \\ Salicylic\ acid. \end{cases}$$

$$\left(Carbazol = \begin{matrix} C_6H_4 \cdot NH_2 \\ | \quad\quad >NH \\ C_6H_4 \cdot NH_2 \end{matrix} \right)$$
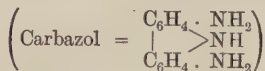
1888. Brownish-yellow powder, giving brownish-yellow solution in water. In concentrated H_2SO_4, violet-blue solution; on dilution, brown ppt.

Application.—A direct cotton colour. Dyes unmordanted *cotton* yellow from an alkaline bath.

CARBAZOTIC ACID, old name for *Picric acid.*

CARBIDE BLACK B, R (S.C.I.). 1899. A direct cotton black.

CARBOLIC ACID *v.* Phenol.

CARBON BISULPHIDE, CS_2.

Preparation. — Bisulphide of carbon is manufactured on a fairly large scale Iron retorts provided with a lining of fireclay and an innermost one of sheet-iron are charged with charcoal, and after being heated to the proper temperature sulphur is added in small portions during a period of twenty hours. More charcoal is then required, and the process recommenced. The vapours pass into suitable condensers. 90 lbs. of charcoal and 400 lbs. of sulphur yield 275 lbs. of crude carbon bisulphide. The raw product is purified by distillation with steam.

Properties.—When pure, carbon bisulphide is a colourless liquid, having a specific gravity of 1·297 at 0° C. It possesses a very strong and disagreeable smell. It is very volatile, and boils at 46° C. Carbon bisulphide is almost insoluble in water, but is miscible with ether and alcohol.

It is an excellent solvent for sulphur, phosphorus, fatty oils, gums, resins, and caoutchouc.

It has been used with more or less success as a volatile scouring agent for wool.

Workmen exposed to the fumes of carbon bisulphide suffer from headache, vomiting, pains in the limbs, and general weakness of mind and body. These affections may develop into actual insanity.

CARBON TETRACHLORIDE, CCl_4. *Tetrachloromethane.*

Preparation. — Carbon tetrachloride is manufactured by passing vapour of carbon bisulphide saturated with chlorine through a red-hot tube. The resulting mixture, which consists of carbon tetrachloride and sulphur chloride, is treated with milk of lime and the carbon tetrachloride separated by distillation. The carbon tetrachloride thus obtained may contain carbon bisulphide. In this case it is necessary to add potash and leave the liquid in contact with it for some time. The tetrachloride may be further purified by washing with water.

Properties. — Carbon tetrachloride is a colourless liquid possessing a pleasant aromatic smell. Its specific gravity is 1·631 at 0° C. It boils at 76° to 77° C., and can be distilled without danger. It is not merely non-inflammable, but extinguishes a flame when poured upon it. It is soluble in alcohol and ether, but does not dissolve in water. Owing to the uninflammable nature of its vapour, it has a great advantage over petroleum spirit as a solvent for oils, fats, tar, grease, paraffin, resins, &c. It is very useful for removing grease stains, differing from petroleum spirit in that no halo remains on the goods after the stain has disappeared. A mixture of carbon tetrachloride and petroleum ether is far less inflammable than petroleum ether alone. Use is made of this mixture together with an addition of 10 grms. soap per litre, which still further lessens the inflammability of the mixture, for cleaning purposes.

The tetrachloride is useful in the caoutchouc industry for brocade printing and bronzing. It combines with benzine soaps, and by suitable treatment can be invested with considerable washing power, which effect may be increased by the addition of ammonium chloride, and acetic acid may be added for preserving certain colours, both these substances being previously mixed with alcohol.

Woollen and silk stuffs dyed with aniline colours, and also various finishing materials do not appear to be affected by carbon tetrachloride.

S. Sommerfeld * has endeavoured to utilise the property possessed by carbon tetrachloride of dissolving fatty colour lakes easily for dyeing silk goods by the so-called dry process.

CARBONISING *v.* Cotton (Action of Acids).

CARDINAL. Mixture of *Chrysoïdine* and *Magenta.* Used for dyeing cotton crimson-red.

CARDINAL S *v.* Acid Magenta S.

CARMINE RED *v.* Cochineal.

CARMINIC ACID *v.* Cochineal.

CARMINNAPHTHE (D. & H.) *v.* Sudan I.

CARMINNAPHTHE J (D. & H.) *v.* Sudan G.

CARMINNAPHTHE GARNET (D. & H.). An azo compound.

Beta-naphthylamine — Beta-naphthol.

1880. Reddish-brown powder, insoluble in water. In concentrated H_2SO_4, magenta-red solution ; on dilution, purplish-brown ppt.

Application.—Used in *calico* printing as a pigment. When produced as an azo colour on cotton is known as *Azo Turkey-red.*

CARMINNAPHTHE GRENAT (D. & H.). An azo compound.

Alpha-naphthylamine — Beta-naphthol.

Red-brown paste, insoluble in water. In concentrated H_2SO_4, blue solution ; on dilution, red-brown ppt.

Application.—Used in *calico* printing.

CARMOISINE (By.) (B.) *v.* Fast Red C (B.).

CARNOTINE (Cl. Co.) *v.* Primuline.

* *Journ. Soc. Chem. Ind.*, 1898, p. 575.

CAROTIN v. CARROTS.

CAROUBIER (D. & H.). Reddish-brown powder. Aqueous solution blood-red; alcoholic solution bluish. Concentrated H_2SO_4, violet solution; on dilution, crimson solution.

Application.—An acid dye. Gives crimson shades on *wool*.

CARROTS (*Daucus carota*) contain a yellow colouring matter, *carotin*, which has been investigated by several chemists. It is insoluble in water or alcohol but soluble in benzine or carbon bisulphide. It has been employed in colouring sweetmeats, &c.

CARTHAMIN v. SAFFLOWER.

CASHMERE v. WOOL.

CASTOR OIL. The seeds of *Ricinus communis* contain 40 to 45 per cent. of oil, which consists principally of triricinoleïn, the triglyceride of ricinoleïc acid, together with some stearin and palmitin.

Castor oil is a colourless liquid which possesses, when fresh, a mild, and afterwards an irritating, taste; it is very viscous, and, when exposed to the air, gradually thickens to a tough mass. It does not dry completely, even in thin layers. The specific gravity is 0·958 to 0·964 at 15° C., according to Allen. It solidifies between −10° and −18° C.

Pure castor oil mixes in all proportions with absolute alcohol and with glacial acetic acid. It dissolves in 2 parts of alcohol of 90 per cent. strength, and 4 parts of alcohol of 84 per cent., but is insoluble in petroleum spirit. Castor oil is saponified analogously to olive oil, the chief product being ricinoleic acid. Turkey-red oil is prepared chiefly from castor oil.

CATECHIN v. CATECHU.

CATECHOL (*Pyrocatechin*),

$$C_6H_4 \left\{ \begin{array}{l} OH\ (1) \\ OH\ (2) \end{array} \right.$$
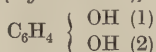
is produced by the dry distillation of those tannins which produce a green coloration with ferric chloride—*e.g.*, *catechu*, *hemlock*, *mangrove*, &c. It is also produced by fusing *phenolorthosulphonic acid* with caustic alkali, or by the reduction of *guaiacol*. It forms white prisms, melts at 104° and boils at 245° C. It is very soluble in water, alcohol, or ether. Its aqueous solution gives a green colour with ferric salts, which changes to violet on adding ammonia. Its alkaline solutions exert a powerful reducing action, and quickly becomes brown by absorption of oxygen.

CATECHU. *Cutch, Gambier.*

Origin.—This dyestuff, which is also known as *Terra japonica*, is obtained from various species of *Mimosa*, *Acacia*, and *Areca*, which are chiefly found in India, and Southern Asia generally. The commercial product is an extract, and is obtained by boiling the wood, twigs, leaves, and fruit of the trees; the following notes * giving a sufficient account of the mode of manufacture :—"The trees are regarded as mature when about a foot in diameter, which occurs when they attain an age of 25 to 30 years. They are then felled, and the bark and outer sapwood is removed and rejected, and after cutting into blocks 2 or 3 feet long the red heartwood is split into chips. The chips are boiled in water for about twelve hours, and the liquor thus obtained is boiled down to a syrup in iron pans with continual stirring. The stirring is continued until the mass is cool enough to be handled, when it is spread on leaves in a wooden frame or mould and allowed to solidify. From the widespread conviction of the necessity for stirring the concentrated solution, it may be inferred that an oxidation is thereby effected. In Baroda the solution is repeatedly squeezed through a blanket and allowed to fall in drops from a height. One ton of dressed timber will yield from 250 lbs. to 300 lbs. of cutch."

The chief commercial varieties of catechu are the following :—

1. **Bombay Catechu**, which is obtained from the heartwood and fruit of the catechu palm, *Areca catechu*. It is imported in large irregular-shaped blocks of a dark brown colour. It has a lustrous fracture, and is almost completely soluble in boiling water, consisting essentially of *catechutannic acid*. Bombay catechu is considered the best quality for dyeing purposes.

2. **Bengal Catechu** is obtained from the unripe fruit and pods and the twigs of *Acacia* and *Mimosa catechu*. It is somewhat lighter in colour than Bombay catechu, and is also sold in large blocks weighing about 1 cwt. This variety contains somewhat less *catechutannic acid*, but more *catechin*, than Bombay catechu, and is therefore less readily soluble.

3. **Gambier Catechu**, also called *cube catechu*, is the product of the leaves of *Uncaria catechu*, a shrub growing chiefly in Batavia. It is sold in the form of small cubes of a dirty brownish-yellow colour. For tanning purposes it is also sold in large blocks, which are soft inside, and are covered with rough matting. Gambier has a dull earthy fracture, and is porous. It is almost insoluble in cold water, and contains very little *catechutannic acid*, consisting essentially of *catechin*.

4. **Kino or Gum Kino** is also a species of catechu, but is of much less importance in dyeing. It is obtained from *Pterocarpus marsupium* and *Butea frondosa*, and occurs commercially as irregular-shaped blocks of a dark reddish-brown colour, and having a very lustrous fracture. It is more employed medicinally than in dyeing or tanning.

* *Indian Pharmacist*, 1896, vol. i., p. 88 (through *Journ. Soc. Chem. Ind.*, 1897, p. 39).

All varieties of catechu have a strongly astringent taste, and are soluble in boiling water or alcohol. Their degree of solubility in cold water depends upon the amount of catechutannic acid contained; and usually the most easily soluble varieties are the best qualities for dyeing purposes. Good qualities should also not contain more than 5 per cent. of ash or 12 per cent. of substance insoluble in boiling alcohol. With gelatine or with sulphuric acid they give brown colorations or bulky precipitates.

Catechu is frequently adulterated with twigs and leaves of the trees, and also with sand, clay, starch, blood, &c.

A dyestuff is also sold under the names of *prepared cutch* or *patent cutch*. It is prepared from gambier by secret processes, which probably consist in treating the liquid gambier with *alum, bichromate of potash*, or *copper sulphate*, these salts being present in the ash from different samples. The presence of these metallic salts modifies the shade produced by the cutch—with alum a yellower, with chrome a redder, and with copper a more olive colour being produced.

Chemistry of Catechu.—Catechu consists mainly of two principles, *catechin* and *catechutannic acid*, along with a brown amorphous substance. These three bodies appear to correspond to three different states of oxidation of one mother substance, *catechutannic acid* being an intermediate oxidation product between the original *catechin* and the brown amorphous ultimate product to which the name *japonic acid* has been applied.

Catechin or *catechuic acid*, when pure, forms white silky crystals, which melt at 217° C., and decompose at higher temperatures with production of *pyrocatechin* ($C_6H_4(OH)_2$) and *protocatechuic acid* $\left(C_6H_3{<}{{(OH)_2}\atop{COOH}} \right)$. It is almost insoluble in cold water, but dissolves easily in boiling water, alcohol, or ether. The aqueous solution is neutral to litmus, and gives a green coloration with ferric chloride, or in presence of sodium acetate an indigo-blue coloration. The formula of catechin is given by Etti as $C_{18}H_{18}O_8$, and, like many other tannins, it yields a red anhydride on *phlobaphene* when heated with dilute sulphuric acid, *pyrocatechin* and *phloroglucin* ($C_6H_3(OH)_3$) being produced at the same time. When fused with caustic alkali it yields the two latter products only, while when boiled with concentrated nitric acid it produces a yellow body analogous to *picric acid*.

Like all phenols, catechin is somewhat easily oxidised, this change occurring slowly by mere exposure to air of its aqueous solution. Oxidation thus occurs during the extraction and evaporation of the extract, and it is probable that this results in the formation of *catechutannic acid* and *japonic acid*. In presence of alkali the oxidation proceeds much more easily, and by treatment with oxidising agents the change to dark brown japonic acid occurs still more rapidly, this production of "japonic acid" forming the basis of the method employed in applying catechu.

Catechin combines with *disazo* compounds, producing new bodies, some of which are employed as dyestuffs.

Catechutannic Acid, the second important principle in catechu, is also known as *mimotannic acid*, the latter name being applied when it is derived from gambier. The composition of this body is somewhat uncertain, but it is probably the first anhydride of catechin, in which case it stands in the same relationship to catechin as does gallotannic acid to gallic acid. It is readily produced by boiling a sodium carbonate solution of catechin, and exists to the extent of 35 to 55 per cent. in catechu and gambier. It differs from gallotannic acid in the reactions tabulated below.

REACTIONS.

	Gallotannic Acid.	Catechutannic and Mimotannic Acid.
Ferrous salts,	White precipitate, gradually becoming blue.	No reaction.
Ferric salts,	Blue coloration or black precipitate, according to dilution.	Greyish-green precipitate.
Tartar emetic,	White precipitate.	No reaction.

Catechutannic acid is easily soluble in water or in alcohol, but is insoluble in dry ether. Like tannic acid, it precipitates solutions of gelatine or tartar emetic. It also produces a greyish-green precipitate with solutions of ferric salts (tannic acid gives a black), and on oxidation it is converted into dark brown japonic acid.

Japonic acid is the name given to the insoluble brown substance produced from *catechin* and *catechutannic acid* by oxidation. Its composition is very uncertain, since it cannot be obtained in a pure condition; possibly it is not a homogeneous substance.

CATECHU BROWN (Ber.). An azo compound.

Bismarck brown $<{{\textit{Phenylene diamine.}}\atop{\textit{Phenylene diamine.}}}$

1887. Dark brown powder, giving brown solution in water. In concentrated H_2SO_4, blackish-brown solution; on dilution, becomes red, then brown, and finally gives a brown ppt.

Application.—A direct cotton colour. Dyes unmordanted *cotton* brown.

CATECHUTANNIC ACID *v.* CATECHU.

CATECHUIC ACID *v.* CATECHU.
CAUSTIC POTASH *v.* POTASSIUM HYDROXIDE.
CAUSTIC SODA *v.* SODIUM HYDROXIDE.
CELESTINE BLUE B (By.) (*Coreïne R R* (D. & H.). An oxazine derivative. 1893. Greenish-black powder, giving red-violet solution in water. In concentrated H_2SO_4, cornflower blue solution, becoming magenta-red on dilution.

Application. — A mordant dye. Dyes chrome-mordanted *wool* bright blue, fast to milling.

CELLULOSE *v.* COTTON.
CERASIN *v.* FAST RED A.
CERASIN (D. & H.) *v.* BORDEAUX B (Ber.).
CERASIN ORANGE G *v.* SUDAN G.
CERASIN RED (C.) *v.* SUDAN III.
CERISE (C.). An impure magenta.
CEROTIN ORANGE C EXTRA *v.* CHRYSOIDIN R.

CHAMOMILE (*Chamomilla matricaria*). The flowers of this plant dye *wool* yellow in conjunction with alum mordant.

CHAY ROOT * (*Oldenlandia umbellata*) is an Indian dyestuff similar to madder, and, like that dyestuff, contains *alizarin* and *purpurin*. "*Al root*" or "*Sooranjee*" (*Morinda citrifolia*) is a similar dyestuff.

CHESTNUT TANNIN. Some confusion appears to exist with regard to the origin of *chestnut extract*, in which form this tannin matter is generally used. It is usually ascribed to the horse-chestnut (*Æsculus hippocastanum*), but is really obtained from *Castanea vesca*. †

The tree is massive, and from 60 to 80 feet in height, the tannin being obtained from the bark and wood. The wood is also employed in the construction of buildings and in cabinet work, and the fruit is a valuable dyestuff. Trimble finds about 8 per cent. of tannin in the air-dried chipped wood, and somewhat less (7·3 per cent.) in the bark, and considers it very probable that the tannin is identical with that from galls—*i.e.*, tannic acid.

Chestnut tannin is almost exclusively used in the form of extract, the liquid extract at about 51° Tw. containing about 55 per cent. solid matter and 15 to 20 per cent. tannin. The solid extract, which is black and lustrous, contains 80 to 90 per cent. solids and 25 to 30 per cent. tannin. ‡

Chestnut extract is largely employed in producing blacks on silk, or on silk and cotton mixed goods.

CHICAGO BLUE B (Ber.). Reddish-blue powder. Aqueous solution, reddish-blue ; alcoholic solution, blue. Concentrated H_2SO_4, greenish-blue, and on dilution becomes violet.

* See "The Colouring Principles contained in Chay root," by A. G. Perkin. *Trans. Chem. Soc.*, 1893, p. 1160, and 1897, p. 817.
† Trimble, *The Tannins.* ‡ *Ibid.*

Application.—A direct cotton dye. Dyes unmordanted *cotton* bright blue.

CHICAGO GREY (G.).

Chicago orange — *Amidonaphthol sulphonic acid G.* 1893.

Application.—A direct cotton dye.
CHICAGO ORANGE (G.). An azo compound.

Nitro amido stilbene disulphonic acid. — *Benzidine.*

1892. Brown powder, giving orange-yellow solution in water. In concentrated H_2SO_4, violet solution ; brown ppt. on dilution.

Application.—A direct cotton colour. Dyes unmordanted *cotton* orange from a neutral salt bath.

CHILI SALTPETRE *v.* SODIUM NITRATE.
CHINA BLUE *v.* SOLUBLE BLUE.
CHINA CLAY *v.* SIZES.
CHINA GRASS. This fibre is also known as *Rhea* or *Ramie*. It is the bast fibre of a species of nettle, *Boehmeria nivea*, with the habit of the common nettle, but without stinging hairs. From the perennial root shoots rise to a height of from 4 to 6 feet. The plant is indigenous to China, but grows well in all sub-tropical countries, and may be grown without difficulty in the South of England.

The name "China grass" was evidently applied to this fibre under the mistaken idea that it was the product of a species of grass, but this is not the case. There are two varieties of the plant, *China grass* proper being from *Boehmeria nivea*, while *Rhea* or *Ramie* is from *B. nivea*, variety *tenacissima*. The former is a much more hardy plant than the latter. In this country, however, the names China grass, Rhea, and Ramie are used indiscriminately.

China grass fibre, when pure, has extremely valuable properties. It far excels all other vegetable fibres in lustre, in which respect it almost rivals silk. It is also very strong and elastic, as is shown by the following comparative figures (Fremerey) :—

	China grass.	Hemp.	Flax.
Strength, . .	100	36	25
Elasticity, . .	100	75	66

Individual China grass fibres have a length of about 20 to 25 c.m. and a diameter of 0·4 to 0·08 mm.

The great obstacle to the extensive use of this valuable fibre resides in the difficulty of separating it from the stem of the plant. The raw fibre is comparatively cheap, but no satisfactory process has hitherto been devised for removing the woody portion and

bark. The process of retting, as used for flax, hemp, and jute, is not suitable, and for close upon a century the chemist and the engineer have unsuccessfully endeavoured to devise a commercially successful process.

The history of this subject is one long series of failure, tempered with sufficient partial success in some cases to encourage future investigators. In 1869 the Indian Government offered a prize of £5000 for a practical solution of the problem. This prize was re-offered in 1881, but no commercially successful process has resulted.

The fibre has long been used in China and India, but it is there separated by hand-picking, a process which is of course unsuitable for a large consumption. It is much more readily separated from the green than from the dried stems.

China grass is very easily bleached, and the purified fibre consists exclusively of cellulose. It is somewhat more difficult to dye than is cotton, but apart from this behaves similarly towards colouring matters.

CHINA GREEN *v.* MALACHITE GREEN.

CHINESE GALLS *v.* GALL NUTS.

CHINESE GREEN *v.* LOKAO.

CHLORAMINE ORANGE (By.). Reddish-brown powder. Aqueous solution, brownish-yellow; insoluble in alcohol. Concentrated H_2SO_4, blue solution; on dilution, reddish-blue, greenish-brown, and finally yellowish-brown.

Application.—A direct cotton dye. Dyes unmordanted *cotton* orange.

CHLORAMINE YELLOW (By.). *Oxyphenin* (Clayton), *Oxyphenin gold* (Clayton), *Thiophosphine J* (L.P.). A primuline oxidation product. Constitution unknown. 1890. Brown-yellow powder, giving yellow solution in water. In concentrated H_2SO_4, blood-red solution; on dilution, brown-yellow ppt.

Application.—A direct cotton colour. Dyes *wool* or unmordanted *cotton* yellow from a neutral bath. Very fast to light.

CHLORANTINE RED 4 B, 8 B (S.C.I.). 1898. Direct cotton colour.

CHLORAZOL BLUE (H.). 1898. A direct cotton blue.

CHLORIDE OF LIME *v.* CALCIUM CHLOROHYPOCHLORITE.

CHLORINE, Cl = 35·5. This element does not occur in nature in the free state, owing to its great affinity for many other substances. In combination as sodium and potassium chloride, it is found in large quantities.

Preparation.—In the laboratory, chlorine is generally made from a mixture of common salt, manganese dioxide, and sulphuric acid with the aid of a gentle heat.

$$MnO_2 + 2NaCl + 2H_2SO_4$$
$$= MnSO_4 + Na_2SO_4 + 2H_2O + Cl_2.$$
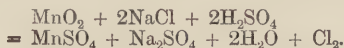
The manufacture of chlorine on the large scale is carried on chiefly in the preparation of bleaching powder. For this purpose the chlorine is obtained by treating manganese dioxide with hydrochloric acid in stone vessels or acid-proof stills.

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2.$$

Chlorine is now prepared in increasingly large quantities with the same object by various electrolytic methods, from brine.

Properties.—Chlorine is a greenish-yellow gas, having a characteristic suffocating smell. It is condensed to a yellow liquid at the ordinary temperature by a pressure of 4 atmospheres. One volume of water absorbs $2\frac{1}{2}$ volumes of chlorine at 15° C. The solution of chlorine in water possesses the same properties as the gas.

Chlorine combines with most metals at the ordinary temperature; antimony and arsenic, when finely powdered, burn spontaneously when thrown into the gas. Chlorine unites with hydrogen with great energy, equal volumes of the gases explode when mixed and exposed to strong sunlight.

$$H + Cl = HCl.$$
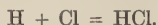
Many hydrocarbons are attacked by chlorine, the hydrogen combining with one-half of the chlorine. A candle burns in chlorine gas with a smoky flame, owing to the formation of hydrochloric acid and separation of carbon.

The action of chlorine as a bleaching agent is due to its affinity for hydrogen. Many organic colouring matters—indigo, litmus, &c. —are decolorised by moist chlorine. It is really the liberation of nascent oxygen by the chlorine which oxidises the colouring matters.

$$H_2O + 2Cl = 2HCl + O.$$
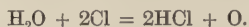
Chlorine acts on cotton with formation of oxycellulose, but prolonged action causes the fibre to become tendered, and eventually decomposes it.

Dry chlorine has little action on wool; dilute solutions of chlorine give up their chlorine to the fibre, causing it to become like silk in feel and to lose its curl and felting power. The power of the wool for absorbing colouring matters, such as naphthol black and green, fast blue, &c., is increased in a remarkable degree by chlorination. Silk, when treated with dilute chlorine solutions, also takes up some dyestuffs with greater avidity, but strong solutions destroy the fibre.

CHLORINE (D. & H.) *v.* DARK GREEN (B.).

CHLOROPHENIN G (Clayton). Closely allied to *Chloramine yellow*, and possesses similar properties.

CHLOROPHENIN ORANGE R, 2 R (Cl. Co.), are similar dyes.

CHROMANIL BLACK B F, 2 B F, 3 B F, R F, 2 R F (Ber.). Direct cotton blacks, after-treated with bichromate of potash.

CHROMATES *v.* Chromium Trioxide.

CHROMAZONE RED (G.). An acid red for wool.

CHROME ALUM *v.* Chromium Sulphate.

CHROME BLUE. C $\begin{cases} C_6H_4 \cdot N(CH_3)_2 \\ C_6H_4 \cdot N(CH_3)_2 \\ C_{10}H_5(OH)COOH \\ OH \end{cases}$

1890. Black paste, slightly soluble in water with a blue colour. In concentrated H_2SO_4, dark red solution, becoming brownish-red on dilution.

Application.—A mordant dye. Used in *calico* printing.

CHROME BORDEAUX (By.) Brownish-red paste. Aqueous solution red, partially soluble only. Alcoholic solution brownish-red. Concentrated H_2SO_4, bluish-red solution; on dilution, brownish-red.

Application.—A mordant dye. Specially suitable for *printing* with acetate of chrome mordant, giving claret-red shades.

CHROME BORDEAUX 6 B DOUBLE (By.). A similar dye, used in wool dyeing on chrome mordant with alum mordant, and in wool dyeing with chrome mordant. On *wool*, gives a very bright blue, fast to milling but not to light.

CHROME BROWN (G.). An azo compound. 1893.

Para-amidophenol disulphonic acid — *Pyrogallol.*

CHROME BROWN R O (M.) *v.* Naphthylamine Brown.

CHROME FAST YELLOW G (Ber.). Yellow powder. Aqueous solution greenish-yellow, alcoholic solution yellow. Concentrated H_2SO_4, brownish-red solution; on dilution, light yellow precipitate.

Application.—A mordant dye. Used in *calico* printing with acetate of chrome mordant, and in *wool* dyeing on bichrome and tartar mordant, giving old gold shades similar to old fustic.

CHROME GREEN *v.* Chromium Hydroxide. A metallic compound.

CHROME GREEN (By.). A coal-tar dye.

C $\begin{cases} C_6H_4 \cdot N(CH_3)_2 \\ C_6H_4 \cdot N(CH_3)_2 \\ C_6H_4 \cdot COOH \\ OH \end{cases}$

1891. Dark brown powder, soluble in water with green-blue colour. In concentrated H_2SO_4, yellow-orange solution.

Application.—A mordant dye. Used in *calico* printing and *wool* dyeing, giving a bright green with chrome mordant.

CHROME ORANGE *v.* Lead Chromates.

CHROME PATENT BLACK T G, T B, T R, T, (K.). Acid mordant dyes. Fixed by "saddening" with bichromate of potash or copper sulphate.

CHROME PATENT GREEN A (K.). Dyed as above.

CHROME PRUNE (By.). Greenish-brown paste. Aqueous solution, brownish-red; alcoholic solution bluish-red. Concentrated H_2SO_4, bluish-red solution; on dilution, brownish-red ppt.

Application.—A mordant dye, giving claret shades with chrome mordant.

CHROME RED R (By.). Red paste. Aqueous and alcoholic solutions, orange-red. Concentrated H_2SO_4, purplish-red solution, becoming orange-red on dilution.

Application.—A mordant dye, used in *calico* printing with acetate of chrome, and producing bright red shades.

CHROME RUBINE (By.). Brownish-red liquid. Aqueous and alcoholic solutions, brownish-red. Concentrated H_2SO_4, yellowish-brown solution; on dilution, gives a brown ppt.

Application. — A mordant dye, giving magenta-red shades with chrome mordant. Used principally in *calico* printing.

CHROME VIOLET, obsolete name for *Rosolan.*

CHROME VIOLET (By.).

C $\begin{cases} C_6H_4 \cdot N(CH_3)_2 \\ C_6H_4 \cdot N(CH_3)_2 \\ C_6H_3 \cdot OH \cdot COOH \\ OH. \end{cases}$

1891. Black paste, insoluble in cold, slightly in hot water. In concentrated H_2SO_4, yellow-brown solution, becoming red-brown on dilution.

Application.—A mordant dye. Used with chrome-mordant in *calico* printing and *wool* dyeing.

CHROME VIOLET (G.).

C $\begin{cases} C_6H_3 \cdot OH \cdot COONa \\ C_6H_3 \cdot OH \cdot COONa \\ C_6H_3 ; OH \cdot COONa \\ OH. \end{cases}$

1889. Chocolate powder. In water, dark red solution. In concentrated H_2SO_4, brown solution, which precipitates on dilution.

Application.—A mordant dye. Used in *calico* printing with chrome mordant.

CHROME YELLOW *v.* Lead Chromate.

CHROME YELLOW D (By.) *v.* Mordant Yellow (B.).

CHROMINE G (K.). See also Thioflavin S. A primuline derivative, produced by methylating and sulphonating primuline base. 1888. Brown-yellow powder, soluble in water. In concentrated H_2SO_4, yellow

6

solution, with blue fluorescence ; on dilution, brown ppt.

Application.—A direct cotton dye, used for *cotton* and *silk*. Dyes greenish-yellow shades from an alkaline bath. Used also in *calico printing*.

CHROMITES v. CHROMIUM.

CHROMIUM, Cr = 52·5. *Chrome iron ore*, FeO,Cr_2O_3, is the chief source of the metal. *Chromate of lead*, $PbCrO_4$, occurs as the mineral *crocoisite*. The metal itself is of little interest, but the compounds of chromium are of great importance as pigments, mordants, and as oxidising agents.

Chromium forms three oxides—CrO, chromium monoxide ; Cr_2O_3, chromic oxide ; CrO_3, chromium trioxide. The two latter compounds are by far the most important. Chromium is trivalent, and acts sometimes as an acid and sometimes as a base. Chromium salts of the latter class have a violet or green colour—*e.g.*, chrome alum and chromic chloride. They are, as a rule, soluble in water, the aqueous solution being acid to litmus. The colour of the solutions changes, on heating, from violet to green, but returns on cooling.

Ammonia precipitates chromium hydrate, $Cr_2(OH)_6$, as a green or purple precipitate, which dissolves in acids.

The chromium salts are not so readily fixed on the cotton fibre as the aluminium salts, as the latter are more unstable.

According to Liechti and Schwitzer [*] neither dilution nor boiling has any effect on normal chromium salts. The more basic the chromium salt the more easily is it dissociated, and the greater the amount of chromium precipitated on the fibre. Solutions of chromium salts are more liable to dissociate after long standing.

CHROMIUM ACETATE, $Cr_2(C_2H_3O_2)_6$ $+ 2H_2O$. The normal salt is obtained by treating lead or calcium acetate with chrome alum, or by adding acetic acid to chromium hydrate until solution is effected. The chromium acetate solution has a violet colour, and does not dissociate on heating. The presence of alkaline hydrates or carbonates and various salts does not cause a precipitate at once in the cold solution, but boiling accelerates the precipitation. The crystals of chromium acetate assume the form of hexagonal tablets, and have the composition mentioned above. Owing to its stability, chromium acetate is somewhat restricted in its application in cotton dyeing, but it is the most valuable chromium compound for printing woollen and cotton goods.

Chromium acetate is met with in commerce in the form of a solution containing about 16 per cent. of the salt.

It may be examined in the same manner as aluminium acetate (*q.v.*).

[*] *Journ. Soc. Chem. Ind.*, 1885, p. 586.

Basic **Chromium Acetates**, $Cr_2(C_2H_3O_2)_5OH$ and $Cr_2(C_2H_3O_2)_2(OH)_4$, together with intermediate compounds, have been prepared by the addition of chromium hydroxide, caustic or carbonate of soda, or ammonia to the normal acetate, or by treating lead or calcium acetate with basic chromium sulphates. These salts dissociate with difficulty, the more basic the salt the greater the tendency to dissociate when diluted and boiled.

Alkaline Chrome Mordant.—For fixing chromium oxide on cotton Koechlin [*] recommends the following mixture to be used :— 2 parts of chromium acetate (25° Tw.), 2 parts of caustic soda solution (66° Tw.), and 1 part of water.

Chromium Chloride Acetates.—These are obtained by dissolving chromium oxychloride (basic chloride) in acetic acid, or by acting on a solution of chrome alum with calcium chloride and calcium acetate. The most basic salts only show signs of dissociation by the combined action of heat and dilution. The salt, $Cr_2Cl(C_2H_3O_2)_2(OH)_3$, yields to the cotton fibre on mordanting, &c., 50 per cent. of its chromium (*Liechti and Schwitzer*).

Chromium Nitrate Acetates.—By evaporating a solution containing 5 equivalents of normal chromium acetate and 1 equivalent of normal chromium nitrate, a salt is obtained which crystallises in green tablets, having the composition $Cr_2(NO_3)(C_2H_3O_2)_4(OH)$. By crystallising this salt from strong acetic acid, the salt $Cr_2(NO_3)(C_2H_3O_2)_5$ is formed.

Preparation.—Chromium nitrate acetates are prepared by double decomposition of the sulphates with lead nitrate and lead acetate. Another method which is recommended by Witz [†] is to reduce potassium bichromate with glycerin in the presence of nitric and acetic acids. The salt, $Cr_2(NO_3)(C_2H_3O_2)_2(OH)_3$, is thus obtained according to the equation—

$$K_2Cr_2O_7 + 3HNO_3 + 2C_2H_4O_2 + 3H_2$$
$$= Cr_2(NO_3)(C_2H_3O_2)_2(OH)_3 + 2KNO_3 + 4H_2O.$$
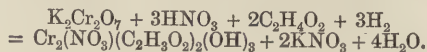
3 kgs. (30 lbs.) crushed potassium bichromate, 4·4 litres (4½ galls.) boiling water, and 26 litres (26 galls.) nitric acid (66° Tw.) are placed in an earthenware vessel standing in the open air. Into this mixture are poured carefully 0·72 litre (3 quarts) white glycerin (48° Tw.), and 4 litres (4 galls.) acetic acid (30 per cent.), half a litre (or ½ gall.) at a time, constantly stirring with a long glass rod. When all the bichromate has dissolved, the mixture is rapidly brought to the boil in a copper boiler until a thin layer of the liquid appears of a fine green colour (about two minutes). An abundant crystallisation of saltpetre is obtained on cooling. The crystals are washed with water, and the

[*] *Journ. Soc. Dyers and Col.*, 1885, p. 18.
[†] A. Renard, *Traité des Matières Colorantes* ; *Journ. Soc. Dyers and Cols.*, 1885, p. 61.

washings are added to the green liquor. About 12 6 kgs. (126 lbs.) (50° Tw.) are obtained.

Chromium nitrate acetates may also be prepared by simply mixing chromium nitrate and chromium acetate in the requisite proportions. Basic salts are obtained by adding sodium carbonate, or by mixing basic salts.

Of the chromium nitrate-acetates, the most basic only are dissociated by heat and by dilution. The salt, $Cr_2(NO_3)(C_2H_3O_2)_2(OH)_3$, is decomposed by the action of heat on a very weak solution, and yields to the cotton fibre 48·5 per cent. of its chromium. The salt, $Cr_2(NO_3)(C_2H_3O_2)(OH)_4$, is decomposed by heat alone, and deposits in the fibre by mordanting 69·1 per cent. of its chromium (*Liechti and Schwitzer*). The chromium nitrate-acetates are employed as mordants in calico printing.

Chromium Sulphate Acetates are prepared by the addition of sodium acetate to chromium sulphate. If the basic sulphates are used basic sulphate acetates are obtained, which are very similar to the chromium sulphates.

The sulphate acetates of chromium resemble the acetates of chromium in their behaviour on dilution and boiling.

CHROMIUM ARSENITE was formerly produced on the fibre as a self colour of a light green shade by treating cotton goods with a chromium salt, and afterwards passing them through a solution of sodium arsenite.

CHROMIUM BISULPHITE. When a solution of a chromium salt is treated with a bisulphite, a yellowish - green solution is formed.

The reaction is probably as follows :—

$$Cr_2(SO_4)_3 + 6NaHSO_3 = 2Cr(HSO_3)_3 + 3Na_2SO_4.$$
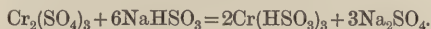
A solution of the compound may be prepared by mixing a concentrated solution of chrome alum with a strong solution of sodium bisulphite until the bluish-green colour has changed to yellowish - green ; an excess of bisulphite is necessary. The solution may be used immediately ; on standing, sodium sulphate crystallises from the solution.

Chromium bisulphite solution yields, on boiling, a basic salt. Steaming or drying promote the decomposition of bisulphite of chromium on the fibre, forming chromium hydroxide, so that it is well adapted for mordanting cotton piece goods.

CHROMIUM CARBONATE is obtained as a greyish-green powder when dilute solutions of chromium salts are precipitated at the ordinary temperature with sodium or ammonium carbonate.

CHROMIUM CHLORATE, $Cr_2(ClO_3)_6$. This salt may be prepared by the double decomposition of chrome alum and barium chlorate. Its solution is violet or green, according to the temperature at which it has

been prepared. A certain amount of barium sulphate always remains in solution, but is precipitated by boiling the solution, or by adding hydrochloric acid.

Chlorate of chromium evolves a distinct odour of chlorine, and when heated to 100°C. gives off large quantities of the gas, becoming transformed into a yellowish-red liquid, containing chromic acid and oxygen compounds of chlorine. The solution soon decomposes.

Chromium chlorate is a powerful oxidising agent. Prudhomme, who describes this salt, has advantageously used a boiling solution of it for making aniline-black ungreenable.

Basic chromium chlorate is used in *calico* printing to produce steam catechu-brown (*oxidation mordant*).

CHROMIUM CHLORIDE, Cr_2Cl_6. If a current of dry chlorine is passed over a heated mixture of charcoal and chromium sesquioxide, violet crystals are produced in the form of a sublimate. A minute quantity of a chromous salt—for example, $CrCl_2$—causes this otherwise sparingly soluble salt to become readily soluble in hot water.

The chromium chloride of commerce is a dark green solution, prepared by treating chrome alum with calcium chloride, or by dissolving the chromic hydrate in hydrochloric acid. Green crystals of the composition $Cr_2Cl_6 + 6H_2O$, and which are deliquescent in the air, crystallise from the solution. On evaporation of the solution basic chlorides and hydrochloric acid are produced. A neutral solution of chromic chloride prepared from the hydrate is used in calico printing.

Basic Chromium Chloride, $CrCl(OH)_2$, is prepared by saturating chromium chloride solution with chromium hydrate, any excess of hydrate being removed by filtration. It is used, like the basic aluminium sulphates, as a mordant for silk and cotton.

Chromyl Chloride, $CrO_2 . Cl_2$, is a blood-red mobile liquid which fumes in air, and is produced by the action of heat on a mixture of common salt, sulphuric acid, and a chromate or bichromate.

CHROMIUM CHROMATE, $Cr_2(CrO_4)_3$. By dissolving chromium hydrate in chromic acid, Gallois (English Patent, 1889, No. 376)* obtained needle-shaped crystals, which, after repeated recrystallisation, gave figures corresponding to the formula $Cr_2(CrO_4)_3 + 9H_2O$.

Basic Chromium Chromate, $Cr_2(CrO_4)_2$ $(OH)_2$, may also be prepared by the action of chromic acid on chromium hydroxide. It dissociates rapidly in solution.

Basic Chromium Sulphate - Chromate, $Cr_2(SO_4)(CrO_4)(OH)_2$, is obtained by dissolving two equivalents of chromium hydroxide, $Cr(OH)_3$, in one equivalent of sulphuric acid and one equivalent of chromic acid—

* *Journ. Soc. Dyers and Col.*, 1889, p. 30.

$$2Cr(OH)_3 + H_2SO_4 + H_2CrO_4 +$$
$$= Cr_2(SO_4)(CrO_4)(OH)_2 + 4H_2O.$$
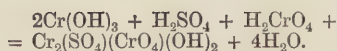
The same compound is formed by double decomposition when two equivalents of $Cr(OH)_3$ are dissolved in two equivalents of H_2SO_4, and the product is acted upon by one equivalent of the normal chromate, or a half equivalent of bichromate of potassium or sodium.

The normal chromium chromate and the basic chromium sulphate-chromate are stable compounds in strong solutions. By boiling or by dilution with water they are dissociated and the chromium hydroxide is precipitated in an insoluble form. The same effect is obtained by subjecting the salts in the fibre to the action of steaming, or by simply washing the fibre.

Under the name of chromium mordants, G. A. I., G. A. II., and G. A. III., certain products are brought into the market by the Farbwerke, vorm. Meister, Lucius & Brüning, which consist of chromium chromate or similar products. To the same class belong the mordants R. E. I., II., and III. for printing, which are issued by the same firm.

Chromium Fluochromate may be prepared by mixing solutions of potassium bichromate and chromium fluoride. A pure product is best obtained by the decomposition of chromium sulphochromate by means of calcium fluoride. It is a useful wool mordant and may in certain cases replace chromium fluoride.

CHROMIUM FLUORIDE, $CrF_3 + 4H_2O$. The commercial salt is a green crystalline powder, containing 42 per cent. Cr_2O_3 (chromic oxide). It is soluble in water, forming a green solution, and is not dissociated by boiling or by dilution. It has a corroding action on glass and on most metals, consequently it must be kept in wooden vessels, and leaden pipes should be used in heating. Chromium fluoride is used as a mordant, both for vegetable and animal fibres.[*] In many instances it can replace the chlorides and acetates, and has no injurious action on the fibre. In calico printing, the results obtained by means of chromium fluoride are superior to those obtained by these mordants.

A mordanting bath of fluoride of chromium can be used continuously. The substance can be advantageously substituted for bichromate in wool dyeing where the oxidising action of the latter is injurious—*e. g.*, for chroming indigo-dyed wool.

Basic chromium fluorides (oxy-fluorides) decompose on evaporation, chromic oxide being separated.

Chromium **Silicofluoride**, $Cr_2F_6 . SiF_4$, has been introduced by Messrs. R. Koepp & Co.

[*] *Journ. Soc. Dyers and Col.*, 1888, pp. 60, 73 ; 1891, p. 121.

as a mordant. It is applied in dyeing and printing in a similar manner to chromium fluoride, and is claimed to give much better results with regard to level dyeing and effectiveness than the latter compound. It can be prepared by acting on chromium hydrate with hydrofluosilicic acid.

CHROMIUM FORMATE is prepared by dissolving moist chromic hydroxide in formic acid of 1·2 sp. gr. It forms dark green crystals, having the formula—

$$Cr(CHO_2)_2 . 2[Cr(CHO_2)_2OH] + 4\tfrac{1}{2}H_2O.$$

The crystals are only slightly soluble in cold, but dissolve more readily in hot water and in hot alcohol.

The aqueous solution does not easily decompose on heating, and is acid to litmus.

Chromium formate can be used like chromic acetate for mordanting cotton in dyeing with alizarin.

CHROMIUM HYDROXIDE, $Cr_2(OH)_6$. *Chromic hydrate.* Is produced by the addition of caustic potash, soda, or ammonia, to solutions of chromium salts. The carbonates of the alkalies form basic salts.

If ammonia be used, the precipitate, though slightly soluble in excess of the reagent (forming a pink solution), is completely thrown down on boiling.

$$Cr_2(SO_4)_3 + 6NH_3 + 6H_2O$$
$$= Cr_2(OH)_6 + 3(NH_4)_2SO_4.$$
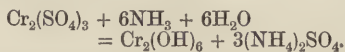
The resulting chromic hydrate is violet-blue if the reagent be in excess ; if too little ammonia has been added the precipitate has a green colour.

On the addition of ammonia to cold solutions of chromium salts, a dark green gelatinous precipitate is produced, but from boiling solutions a light green powdery precipitate is obtained. On drying the precipitate at 100° C. it becomes greyish-black, and has the composition—

$$Cr(OH)_3 . H_2O, \text{ or } Cr(OH)_3 . 5H_2O.$$
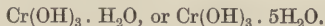
Tartaric, citric, and oxalic acids or sugar tend to prevent the precipitation of the hydrate, and sometimes cause it to re-dissolve on standing, forming red solutions.

If excess of caustic potash or soda is used, the precipitate dissolves with an emerald-green colour, but is completely re-precipitated by continued boiling, the supernatant liquid being colourless. An addition of ammonium chloride has the same effect. The alkaline carbonates dissolve chromium hydrate sparingly. On heating chromium hydroxide to 200° C. in a current of hydrogen, the *hydroxide*, $CrO(OH)$, and on further heating chromic oxide (Cr_2O_3) is formed.

Chromium hydrate strongly resembles aluminium hydrate. It forms with acids the *chromium salts*, but with caustic potash and

soda it forms *chromites*, acting in the latter case as a weak acid.

Guignet's Green, $Cr_2O(OH)_4$, is produced by melting boric acid with potassium bichromate. It is insoluble in water, and only slowly attacked by boiling acids.

Chrome Green.—Chrome green consists chiefly of chromium hydroxide. The hydroxide yields a very light shade of sea green, hardly visible in artificial light, and rarely used now. Formerly a *chromium arsenite* was produced on the fibre by mordanting with a chromium salt, and then passing through a hot solution of arsenite of soda. This process yields a moderately full and very fast green, which does not appear very different when seen by daylight or by artificial light; but its poisonous character renders its use objectionable. Phosphate and silicate of soda have similar effects, but give inferior results. Chromium oxide can be produced on cotton by the usual mordanting methods, and on wool by saturating the fibre with a hot or cold strong solution of bichromate, and then passing the material through sodium bisulphite; by repeating the process fuller colours are obtained. The colour known on cotton as "khaki" may be produced by precipitating on the fibre a mixture of chromic and ferric hydrates.

CHROMIUM NITRATE, $Cr_2(NO_3)_6$. If potassium bichromate be reduced in presence of nitric instead of sulphuric acid, chromium nitrate is produced. It may also be prepared by the action of lead nitrate on chrome alum, or by dissolving chromic hydrate in nitric acid.

By careful manipulation, violet crystals of the salt containing 9 molecules of water may be separated, but the solution generally yields an amorphous green mass. The substance is not extensively used. It is sold as a blue solution, which appears red by transmitted light.

By the addition of chromic hydrate, sodium hydrate, &c., to the solution, basic salts are obtained. The nitrates behave similarly to the sulphates and chlorides; the sulphates appear to be the most stable of the three, and the nitrates the most easily dissociated.

Both the normal and basic nitrates of chromium are used as mordants for cotton.

CHROMIC OXIDE. *Chromium sesquioxide,* Cr_2O_3. Chromic oxide is formed by heating chromic hydrate. It is a green amorphous powder, not easily soluble in acids. It is used under the name of *chrome green* as a pigment, and is very permanent. The oxide has been prepared in the form of green crystals by passing vapour of chromyldichloride (CrO_2Cl_2) through a red-hot tube.

CHROMIUM PHOSPHATE, $CrPO_4$. Sodium phosphate, on being added to solutions of chromium salts, precipitates this compound as a dark green mass, which becomes dark blue on drying. The phosphate may also be obtained as violet crystals, having the composition $CrPO_4 + 6H_2O$. Long continued boiling is necessary if chromium acetate be used.

Phosphoric acid dissolves chromium hydrate, the solution yielding, on evaporation and heating the residue to 316° C., a green chromium metaphosphate, $Cr(PO_3)_3$, which is insoluble in water and in acids.

CHROMIUM SULPHATE, $Cr_2(SO_4)_3$. Sulphuric acid dissolves chromium hydrate, forming a green solution, which, after long standing, deposits a mass of greenish-blue crystals. Violet-blue crystals (octahedra), of the composition $Cr_2(SO_4)_3 + 15H_2O$, can be eventually obtained by re-crystallising the crude product from dilute alcohol.

The aqueous solutions of chromium sulphate have a violet or green colour; the violet solutions become green on boiling. Barium chloride precipitates the whole of the sulphuric acid from the cold violet solutions, but only after prolonged boiling from the green solutions.

Solutions of chromium sulphate give precipitates on addition of caustic soda or the phosphates, arsenates, silicates, and carbonates of the alkalies. The precipitate is soluble in an excess of caustic soda, and in a large excess of ammonia, but boiling causes its re-precipitation.

By the addition of sodium hydrate or chromium hydrate to solutions of the normal sulphate or of chrome alum, basic chromium sulphates result. A number of basic salts have been prepared, which vary in stability according to the degree of basicity and the presence of alkaline salts. Boiling does not dissociate the basic salts, but dilution has that effect; the more basic they are the more easily they are decomposed.

A solution of normal chromium sulphate is not decomposed by either heating or dilution, or the combined action of heat and dilution. Chromium sulphate is not used as such, but in combination as chrome alum.

Chrome Alum—

$$Cr_2(SO_4)_3 . K_2SO_4 + 24H_2O.$$

Preparation.—Chrome alum is produced in a pure state when a mixture of potassium bichromate and sulphuric acid is treated with a reducing agent, such as sulphurous acid, alcohol, starch, or sugar.

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 + 23H_2O$$
$$= Cr_2(SO_4)_3K_2SO_4 + 24H_2O$$
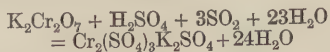
It is also obtained in an impure condition (containing tarry matter, sulphuric acid, and calcium sulphate) as a by-product in the manufacture of some colouring matters—viz., alizarin.

It can be prepared by dissolving 2 lbs. of bichromate of potash in 1 gallon of water and 3 lbs. of sulphuric acid. The mixture is heated to 35° C., and alcohol slowly added until the colour of the solution becomes dark green. The chrome alum crystallises (preferably from acid solutions) in dark violet octahedra. The crystals are soluble in 7 parts of cold water, forming a violet solution, which becomes green on heating to about 65° C. Barium chloride precipitates all the sulphuric acid from the violet solution at the ordinary temperature, but only after prolonged boiling from the green solution. Chrome alum is insoluble in absolute alcohol. The crystals contain 39·3 per cent. of $Cr_2(SO_4)_3$, which is equivalent to 15·3 per cent. of Cr_2O_3.

The basic salts obtained from chrome alum do not suffer dissociation so quickly as those obtained from the pure chromium sulphate, the presence of alkaline sulphates causing increased stability. Chrome alum is used in calico printing, dyeing, tanning, and in the preparation of other chromium compounds.

Analysis. — *Chromic oxide* may be determined by precipitation with ammonia, similarly to alumina in potash alum.

CHROMIUM SULPHOCYANIDE or THIOCYANATE, $Cr_2(CNS)_6$.

Preparation.—Hydrosulphocyanic acid dissolves chromium hydrate, forming a green-violet liquid, from which a dark green amorphous salt separates. This substance is deliquescent, and has the composition $Cr_2(CNS)_6$.

On the large scale, chrome alum is decomposed by means of barium or calcium sulphocyanide. Solutions of the normal salt do not dissociate either on heating or diluting.

Double salts of the sulphocyanides—*e.g.*, *potassium chromium sulphocyanide*, $Cr(CNS)_3$ + $3K(CNS)$ + $4H_2O$—also exist.

By the addition of chromium hydroxide or sodium hydroxide to the normal salt, basic salts of considerable stability are formed.

The normal salt yields only about 5 per cent. of chromium to the cotton fibre, the basic salt, $Cr_2(CNS)_2(OH)_4$, about 34 per cent. of the available chromium.

There is a difference of opinion as to whether chrome alum or chromium sulphocyanide is the better mordant.

Sulphocyanide of chromium is used by calico printers for the production of steam logwood blacks, which are characterised by their great brilliancy and fastness. Lauber (*Handbuch des Zeugdrucks*) considers it an excellent mordant for print colours. It behaves in the same way towards the fibre as the corresponding aluminium salt, having no injurious action on it.

Analysis.—The determination of sulphocyanic acid is carried out, according to Watson Smith,[*] as follows :—To a known weight of the solution is added sodium bisulphite and then copper sulphate solution. On warming, cuprous sulphocyanide is precipitated. This is filtered off, washed well, and ignited cautiously with the addition of sulphur in a Rose's crucible, hydrogen gas being passed through the tube in the crucible lid to displace air. The cuprous sulphide, Cu_2S, is then weighed, and from the Cu the sulphocyanic acid is calculated. An alternative method is as follows :—A filter paper is dried in the water-bath until of constant weight, a stoppered tube being used during cooling and weighing. The precipitate of cuprous sulphocyanide is collected and washed on this filter paper, and eventually dried until of constant weight, using the stoppered tube as before. The gain in weight of the filter paper and tube is the amount of cuprous sulphocyanide, from which the weight and proportion of sulphocyanic acid are readily calculated. 121·7 parts $Cu(CNS)$ contain 58·1 parts (CNS).

CHROMIUM TRIOXIDE.
Chromic Anhydride, Chromic Acid, CrO_3. This substance is prepared by adding an excess of concentrated sulphuric acid to a strong solution of potassium bichromate.

$$K_2Cr_2O_7 + H_2SO_4 = 2CrO_3 + K_2SO_4 + H_2O.$$

Crimson crystals of chromic oxide are formed on cooling, the liquid being decanted and the crystals drained on porous plates. On heating to 250° C. the crystals evolve oxygen, and at higher temperatures are converted into Cr_2O_3. Chromic anhydride is very soluble in water, forming a solution of "chromic acid," H_2CrO_4.

Chromic anhydride is a very powerful oxidising agent, and is used as such both in the laboratory and in various manufacturing processes—*e.g.*, in the preparation of alizarin.

Reducing agents re-act violently upon the dry crystals, alcohol even taking fire, and sulphuretted hydrogen, sulphur dioxide, and many organic substances being more or less completely oxidised.

$$2CrO_3 + 3SO_2 + 3H_2O = Cr_2(SO_4)_3 + 3H_2O.$$
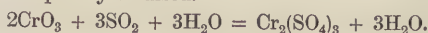
By the action of strong acids on chromium trioxide, oxygen is evolved, and chromic salts are formed. It behaves like a peroxide towards hydrochloric acid, chlorine being set free.

$$2CrO_3 + 12HCl = Cr_2Cl_6 + 6H_2O + 3Cl_2.$$
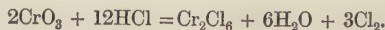
CHROMATES.

Chromate of Ammonium *v.* AMMONIUM CHROMATE.

Chromate of Potash. *Potassium Chromate,* K_2CrO_4, *Yellow* or *Neutral Potassium Chro-*

mate. This substance is prepared from chrome iron ore, $FeO . Cr_2O_3$, or by neutralising bichromate of potash with potassium hydrate. It crystallises in yellow rhombic prisms, which are very soluble in water. 100 parts of water at the ordinary temperature dissolve about 60 parts of the salt. Its general properties are similar to those of the bichromate into which it is easily converted by the addition of acids.

$$2K_2CrO_4 + H_2SO_4 = K_2Cr_2O_7 + K_2SO_4 + H_2O.$$

Bichromate of Potash. *Potassium Bichromate*, $K_2Cr_2O_7$, *Red Chromate of Potash, Bichrome or Chrome.*

Preparation. — Finely - powdered *chrome iron ore* ($FeOCr_2O_3$) is mixed with lime and heated in furnaces. Oxide of iron and calcium chromate, $CaCrO_4$, are formed, the latter compound being dissolved by means of dilute sulphuric acid, and thus producing calcium bichromate, $CaCr_2O_7$. On treating the bichromate of calcium with potassium carbonate, potassium bichromate is obtained.

$$CaCr_2O_7 + K_2CO_3 = K_2Cr_2O_7 + CaCO_3.$$
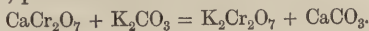
Properties.—Bichromate of potassium crystallises in large orange-red triclinic prisms. It melts on heating, and at high temperatures gives off oxygen.

$$2K_2Cr_2O_7 = 2K_2CrO_4 + Cr_2O_3 + 3O.$$

The salt contains no water of crystallisation, and is stable in the air. 100 parts of water at the ordinary temperature dissolve about 10 parts, and at 100° C. about 94 parts of the substance.

Potassium bichromate is poisonous, and has a bitter metallic taste.

In the presence of organic bodies bichromate of potash is reduced. If wool which has been mordanted with this salt be exposed to light, the yellow colour changes to green, so that if the wool has not been evenly exposed uneven dyeing will result.

Bichromate of potash is the most important of wool mordants, and is used in cotton dyeing in the production of aniline black, chrome yellow, cutch brown, &c. It is also an ingredient of many chrome pigments, and is the raw material for the production of all other chromium compounds. It is employed for oxidising anthracene in the manufacture of alizarin and as a bleaching agent for decolorising oils.

Commercial potassium bichromate is usually almost chemically pure, although sometimes potassium sulphate is present, owing to imperfect manufacture, since the potassium sulphate and the bichromate have evidently crystallised simultaneously. The analysis is carried out similarly to that of sodium bichromate.

Bichromate of Soda. *Sodium Bichromate*, $Na_2Cr_2O_7$.

Preparation.—*Sodium chromate*, Na_2CrO_4 + $10H_2O$, is prepared from chrome iron ore by fusing with soda ash and chalk, the mass is lixiviated and the solution crystallised. The crystals of sodium chromate are dissolved in water and treated with sulphuric acid, and afterwards sufficient of the neutral sodium chromate added to bring the percentage of CrO_3 to about 72·5. The sodium sulphate is crystallised out by cooling and the mother liquor evaporated to dryness.

Properties.—The salt is deliquescent, especially if it contains an excess of CrO_3 above the amount mentioned above. It is readily soluble in water, from which it crystallises in red six-sided prisms, having the composition $Na_2Cr_2O_7 . 2H_2O$.

The commercial product, which is cheaper than the potassium salt, comes into the market (1) in the form of crystals containing 2 molecules = 12 per cent. of water of crystallisation, (2) in lumps or as a powder of the fused and partially dehydrated compound. The amount of $Na_2Cr_2O_7$ varies from 84 to 98 per cent.

It has an acid reaction and a bitter metallic taste. It loses 1 molecule of water on heating to 75° C., and it forms a light brown anhydrous mass when dried at 100° C. It melts at 320° C., and above this temperature commences to decompose, consequently the fused products always contain more or less chromic oxide.

The anhydrous salt dissolves in water, causing a rise of temperature, while the hydrated salt causes a depression of temperature when treated with water.

100 parts of water dissolve at 15° C. 109 parts and at 100° C. 163 parts of sodium bichromate ($Na_2Cr_2O_7$).

Sodium bichromate in the form of crystals with 2 molecules of water is nearly equivalent to the (anhydrous) potassium bichromate, the molecular weights of these two salts being 299 and 295 respectively; the equivalent of the anhydrous sodium salt is 263 in round numbers.

Sodium bichromate is used in place of potassium bichromate on account of its lower price and its greater solubility. It can, in nearly every case, replace the potassium salt perfectly. There is, however, some difference in the action of the two salts as wool mordants which has not yet been explained.

The crude varieties of sodium bichromate often contain considerable quantities of normal chromate (which is a much less effective mordant than the acid salt), sodium sulphate, and other impurities.

Analysis.—Estimation of Chromic Acid.— The usual method of estimating chromic acid in chromates and bichromates consists in adding in excess a known quantity of ferrous ammonium sulphate to an acidulated solution

of the sample and titrating the residual ferrous salt with decinormal potassium bichromate. In lieu of this mode of procedure, the following plan can be recommended:—Weigh out 5 grms. of the sample and dissolve in a litre of water, with which solution fill a burette. In the case of sodium bichromate, in order to obtain a fair average sample, it is preferable to weigh out 25 grms. and dissolve in 500 c.c., and then, after shaking, take out 100 c.c. and dilute to a litre. One grm. of pure ferrous ammonium sulphate is then weighed out and dissolved in a little water in a porcelain basin, and 50 c.c. of a 10 per cent. solution of sulphuric acid added. The solution of bichromate is then added during constant stirring with a glass rod until a drop of the liquid ceases to give a blue or greenish-blue coloration when brought in contact with a drop of potassium ferricyanide solution on a porcelain slab. One grm. of ferrous ammonium sulphate reduces 0·0854 grm. of CrO_3; consequently, the number of c.c. of the solution required contains this amount of chromic acid.

Example. — 5 grms. of potassium bichromate were dissolved in a litre of water. Of this solution, 1 grm. of ferrous ammonium sulphate required 25·2 c.c.

∴ 25·2 c.c. = 0·0854 grm. of CrO_3.

∴ 1000 c.c. = 3·388 grms. of CrO_3.

$$\frac{3 \cdot 388 \times 100}{5} = 67 \cdot 76 \text{ per cent. of } CrO_3.$$

Crystallised sodium bichromate ($Na_2Cr_2O_7 + 2H_2O$) contains, when pure, nearly the same amount of chromic acid as potassium bichromate—viz., 67·70 per cent.

Chromic acid may be determined *gravimetrically* by conversion either into chromic oxide or chromate of lead. The former process is carried out by dissolving 0·5 grm. of the sample of bichromate in a little water (or by taking 100 c.c. of the solution mentioned above) adding hydrochloric acid, and heating either with alcohol or sulphurous acid. The excess of either of these reducing agents is boiled off and the green solution diluted to about 200 c.c., and treated with a *slight* excess of ammonia. The precipitate is collected on a filter, well washed, dried, ignited, and weighed as Cr_2O_3; 153 parts of Cr_2O_3 correspond to 201 parts of CrO_3.

Estimation of Normal Chromate.—Potassium bichromate rarely contains normal chromate, but, as previously stated, the sodium compound frequently contains considerable quantities. Formerly this was more frequently the case than at present. Three methods for estimating normal chromate will be described, but, when present in small quantities, preference is given to the first process.

1. M'Culloch's process [*] depends upon the fact that free chromic acid, when shaken up with peroxide of hydrogen and ether, imparts a blue coloration to the ether, whereas neither chromate nor bichromate produce the effect. If bichromate alone is taken, a drop or two of acid is sufficient to produce the blue colour, whereas, if normal chromate is present, acid must be added in sufficient quantity to convert it into bichromate. The following plan of carrying out the operation is recommended :—2·5 to 5 grms. of the sample are dissolved in 50 c.c. of water, and the solution introduced into a stoppered cylinder holding about 120 c.c. ; 10 c.c. of hydrogen peroxide (10 vols.) and about 20 c.c. of ether are added and the contents shaken. (If free chromic acid be present, the ethereal layer will be of a blue colour.) A decinormal solution of sulphuric acid is now added in small quantities at a time with frequent agitation until the ether is tinged faintly blue, which is best seen against a white background. Each c.c. of $\frac{N}{10}$ acid corresponds to 0·01005 grm. of CrO_3 as normal chromate = 0·01625 grm. of Na_2CrO_4, or 0·01945 grm. of K_2CrO_4. If the hydrogen peroxide contains acid this must be taken into account.

2. In the paper above mentioned, M'Culloch refers to the direct determination of bichromate by means of standard soda and phenolphthaleïn, and thence by deducting chromic acid so found from the total chromic acid, calculating the amount of normal chromate present. He correctly points out that the end reaction is not sharp and precise, but if an excess of standard soda be added and the liquid titrated back with standard acid this difficulty is altogether overcome. 1 c.c. of $\frac{N}{10}$ soda = 0·01005 grm. of CrO_3 as bichromate.

3. R. T. Thomson[†] has shown that bichromate of potash or soda is neutral to lackmoid, whilst normal chromate is alkaline. Normal chromate may, therefore, be estimated in bichromates by standard acid and lackmoid paper. Free chromic acid may be likewise determined by using decinormal soda.

Examples. — A sample of impure bichromate of soda gave 70·60 per cent. of total chromic acid, CrO_3.

By Method 1.—2·5 grms. with hydrogen peroxide and ether required 30·6 c.c. of $\frac{N}{10}$ sulphuric acid.

$$\therefore \frac{0 \cdot 01005 \times 30 \cdot 6 \times 100}{2 \cdot 5}$$

$$= 12 \cdot 30 \text{ per cent. of } CrO_3 \text{ as chromate.}$$

∴ by difference = 58 per cent. of CrO_3 as bichromate.

* *Chem. News*, vol. lv., 1887, p. 2.
† *Ibid.*, vol. lii., 1885, p. 29.

By Method 2.—50 c.c. of a 1 per cent. solution (= 0·5 grm.) were treated with a few drops of phenolphthaleïn and 35 c.c. of $\frac{N}{10}$ caustic soda. 6·1 c.c. of $\frac{N}{10}$ acid were then required to produce a pure yellow solution.

$$\therefore \frac{0 \cdot 01005 \times 28 \cdot 9 \times 100}{0 \cdot 5}$$

= 58·08 per cent. of CrO_3 as bichromate, and by difference = 12·52 per cent. CrO_3 as chromate.

By Method 3.—100 c.c. of a 1 per cent. solution (= 1 grm.) were titrated with $\frac{N}{10}$ sulphuric acid, using lackmoid paper as an indicator. 12·6 c.c. were required.

$$\therefore 0 \cdot 01005 \times 12 \cdot 6 \times \text{ by } 100$$

= 12·66 per cent. of CrO_3 as chromate, and by difference = 57·94 per cent. of CrO_3 as bichromate.

Sulphuric acid as potassium or sodium sulphate in bichromates is most accurately determined by reducing the chromic acid to chromic oxide by means of alcohol and hydrochloric acid in dilute solutions, and precipitation with barium chloride.

Chromites. The alkaline chromites have not been prepared in the solid state. A solution of sodium chromite may be obtained by dissolving chromic hydrate in excess of caustic soda.

$$Cr_2(OH)_6 + 6NaOH = Cr_2(ONa)_6 + 6H_2O.$$
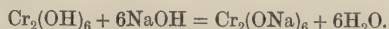
Ammonium salts and dilute acids, including carbonic acid, decompose the chromites. If a textile fibre be present in the mixture, the decomposition takes place still more rapidly, chromic oxide being deposited. The chromites dissolve cupric and ferric oxides.

Chromyl Chloride *v.* CHROMIUM CHLORIDE.

CHROMOCYANINE V, B (D. & H.). 1889. A mordant dye, giving bright blues on wool and cotton.

CHROMOGEN I (M.). Sodium salt of chromotrope acid (*1 : 8 dioxynaphthalene, 3 : 6 disulphonic acid*), 1891. Dirty white powder, soluble in water.

Application.—Applied to *wool* as an acid dye, a brown being subsequently developed on the colourless wool by oxidation with bichromate solution.

CHROMOPHOR or CHROMOPHOROUS GROUP. A term used to designate that portion of the molecule of a colouring matter upon which their colour-producing property depends ; *v.* also COAL-TAR COLOURS.

CHROMOTROPES (M.). Azo compounds, containing the chromotrope acid.

OH OH

R

NaSO₃   SO₃Na.
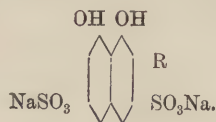
Discovered
in 1890.

Application. — Dyed as ordinary acid colours, producing bright red to violet colours, many of which are very fast to light. By a subsequent treatment with bichromate the reds are developed into blues or blacks, the action being due partly to oxidation and partly to formation of a chrome lake.

CHROMOTROPE 2 B (M.). 1890. An azo dye.

Chromotrope acid — Paranitraniline.

Red - brown powder, giving yellowish - red solution in water. In concentrated H_2SO_4, dark violet solution, becoming red on dilution. *Colour as dyed*, bluish-red ; *developed colour*, navy-blue to blue-black.

CHROMOTROPE 6 B (M.). 1890. An azo dye.

Chromotrope acid — Para-amidoacetanilid.

Grey-brown powder, giving violet-red aqueous solution. In concentrated H_2SO_4, magenta-red solution ; on dilution, blue-red ppt. *Colour as dyed*, violet-red ; *developed colour*, navy-blue.

CHROMOTROPE 8 B (M). 1890. An azo dye.

Chromotrope acid — Naphthionic acid.

Grey-violet powder, giving violet solution in water. In concentrated H_2SO_4, indigo - blue solution ; violet, on dilution. *Colour as dyed*, red-violet ; *developed colour*, purplish navy-blue.

CHROMOTROPE 10 B (M.). 1890. An azo dye.

Chromotrope acid — Alpha-naphthylamine.

Brownish-violet powder, giving brown aqueous solution. In concentrated H_2SO_4, greenish-blue solution, becoming red-violet on dilution. *Colour as dyed*, violet ; *developed colour*, purplish navy-blue.

CHROMOTROPE F B (M.). 1894. *Colour as dyed*, bright crimson ; *developed colour*, dark violet.

CHROMOTROPE 2 R (M.). 1890. An azo dye.

Chromotrope acid — Aniline.

Brownish-red powder, giving magenta-red solution in water. In concentrated H_2SO_4, magenta-red solution, becoming yellow-red on dilution. *Colour as dyed*, bright red ; *developed colour*, violet-black.

CHROMOTROPE S (M.). *Colour as dyed*, brownish - violet ; *developed colour*, violet-black.

CHROMOTROPE S B (M.). *Colour as dyed*, dark violet ; *developed colour*, bluish-black.

CHROMOTROPE S R (M.). *Colour as dyed*, violet-brown ; *developed colour*, blackish-violet.

CHROMYL CHLORIDE *v.* CHROMIUM CHLORIDE.

CHRYSAMINE G (By.) (Ber.) (L.) (Lev.). *Flavophenin* (B.). An azo compound.

$$Benzidine\begin{cases}Salicylic\ acid.\\Salicylic\ acid.\end{cases}$$

1884. Brown powder, very slightly soluble in water. In concentrated H_2SO_4, reddish-brown solution; on dilution, brown ppt.

Application. — A direct cotton colour. Dyes unmordanted *cotton* yellow from a soap bath. Fast to light.

CHRYSAMINE R (By.) (Ber.) (L.) (Lev.). An azo compound.

$$Tolidin\begin{cases}Salicylic\ acid.\\Salicylic\ acid.\end{cases}$$

1884. Yellowish-brown powder, soluble in water. In concentrated H_2SO_4, reddish-violet solution; on dilution, brown ppt.

Application.—As CHRYSAMINE G.

CHRYSANILINE *v.* PHOSPHINE.

CHRYSAUREÏNE *v.* ORANGE II.

CHRYSENE *v.* Anthracene.

CHRYSEOLINE *v.* RESORCIN YELLOW.

CHRYSOÏDINE, *all makers.* *Chrysoïdine G* (D. & H.) (G.), *Chrysoïdine R* (C.), *Chrysoïdine* (S.C.I.), *Chrysoïdine Y* (Lev.). An azo compound.

Aniline — Meta phenylene diamine.

1875. Red-brown crystalline powder or large shining black crystals, giving orange-brown solution in water. In concentrated H_2SO_4, brownish-yellow solution, becoming cherry-red on dilution.

Application.—A basic colour. Dyes *wool*, *silk*, or tannin-mordanted *cotton* orange. Used also in *leather* dyeing.

CHRYSOÏDINE R (S.C.I.) (G.) (Lev.). *Gold-orange for cotton* (D. & H.), *Cerotin-orange C extra* (C.I.). An azo compound.

Aniline — Meta toluylene diamine.

Yellowish-brown lumps, giving orange solution in water. In concentrated H_2SO_4, greenish-yellow solution, becoming blue-red and then yellow-red on dilution.

Application.—As CHRYSOÏDINE G.

CHRYSOÏDINE R (D. & H.). An azo colour.

Orthotoluidine — Meta toluylene diamine.

Violet crystalline powder, giving red solution in water. In concentrated H_2SO_4, brown solution; on dilution, slimy ppt.

Application.—As CHRYSOÏDINE G, but gives browner shades.

CHRYSOÏN *v.* RESORCIN YELLOW.

CHRYSOLIN (Mo.). A fluoresceïne derivative. *Sodium salt of benzylfluoresceïne.* 1877. Red-brown powder or lumps smelling of benzylchloride. In water, brown solution with green fluorescence. In concentrated

H_2SO_4, yellow, slightly fluorescent solution; on dilution, yellow ppt.

Application.—Dyes *silk* yellow from neutral (or acetic) acid bath.

CHRYSOPHENIN (L.) (Ber.) (By.). An azo compound.

$$Diamido\ stilbene\ disulphonic\ acid\begin{cases}Phenol.\\Phenetol\end{cases}$$

1886. Orange-yellow powder, slightly soluble in cold, easily in hot water. In concentrated H_2SO_4, reddish-violet solution; blue ppt. on dilution.

Application.—A direct cotton dye. Dyes unmordanted *cotton* yellow from a soap bath.

CINCHONA BARK, after the extraction of the quinine, if distilled with caustic soda, and the oil thus obtained treated with amyl iodide, yields a blue dye, which is employed for orthochromatising photographic plates, staining botanical sections, &c.

CINNAMON BROWN *v.* BISMARCK BROWN.

CINEREÏNE (P.). An induline, obtained from *azoxyaniline, aniline hydrochloride,* and *paraphenylene diamine.*

Application.—See INDULINE.

CITRATES *v.* CITRIC ACID (*Analysis and Valuation*).

CITRIC ACID, $C_6H_8O_7$ ($= C_3H_4(OH)(COOH)_3$) + H_2O.

Preparation.—Citric acid exists in the juice of lemons, limes, oranges, and other fruits; it is obtained from the juice of lemons (or lime-fruit) which comes into commerce from Southern Europe and the West Indies. The lime-juice is boiled (to coagulate albuminoids), filtered, and saturated with chalk and milk of lime. The calcium salt which separates is decomposed by means of sulphuric acid, and the filtrate evaporated and crystallised.

Citric acid crystallises in prisms with 1 molecule of water of crystallisation, which melt at 100° C., lose water, and the anhydrous salt then melts at 153° C. It dissolves in three-quarters its weight of water at 15° C. and in twice its weight of alcohol.

Citric acid is a tribasic acid; the salts are known as *citrates.* The acid is used as a resist and discharge in printing. Commercial citric acid consists of large crystals, which often have a yellowish tinge, but do not contain any considerable quantity of impurities. A good acid should leave no ash when incinerated.

Analysis.—*Citric acid* in the free state is estimated by titration with normal soda and phenolphthaleïn.

1 c.c. $\frac{N}{1}$ alkali = 0·07 grm. of crystallised citric acid, $C_6H_8O_7 + H_2O$.

Citric acid is liable to the same impurities and adulterations as tartaric acid (*q.v.*).

Both tartaric and citric acids are often

contaminated with metallic *lead* and *lead compounds*, owing to their preparation in leaden vessels.

M. Bucket * estimates *metallic lead* as follows :—

200 grms. of the acid are dissolved in 600 c.c. of water and ammonia is added in slight excess, so as to effect the perfect solution of any crystalline lead sulphate present. After leaving twenty-four hours, the supernatant liquid is decanted and set aside, any residue being carefully washed on a filter. The residue is dissolved in nitric acid, the solution concentrated and mixed with concentrated sulphuric acid, and then with twice its volume of alcohol. The precipitated lead sulphate is washed with alcohol, dried, ignited, and weighed.

The solution of ammonium citrate (or tartrate) first obtained serves for the detection of *compounds of lead*. The solution is acidulated with hydrochloric acid, precipitated with sulphuretted hydrogen water, and the lead determined as $PbSO_4$ by dissolving the PbS in nitric acid as above.

Citric acid was formerly often found adulterated with tartaric acid, but, on account of the price, this method of sophistication is now practically obsolete.

Tartaric acid, however, may readily be detected by treating the sample with concentrated sulphuric acid and heating the mixture in the water-oven for about half an hour. Pure citric acid undergoes practically no change, whereas tartaric acid blackens. One per cent. of tartaric acid in citric acid may be thus detected. For determining the amount of tartaric acid in citric acid, Allen's † process is to be recommended. It depends upon the precipitation of acid potassium tartrate by a solution of potassium acetate in proof spirit.

Oxalic acid may be detected by neutralising with ammonia and adding acetic acid and calcium chloride, when, if present, a precipitate of calcium oxalate will be formed.

CITRONINE (D. & H.) *v.* CURCUMEÏNE.

CITRONINE (Br. S. & Sp.). A nitro compound. *Tetra nitrodiphenylamine.* 1878. Now obsolete. A yellow acid dye.

CITRONINE (F.) *v.* AZO YELLOW.

CITRONINE A (L.) *v.* NAPHTHOL YELLOW S.

CLAYTON CLOTH RED (Cl. Co.). *Stanley red* (Cl. Co.). An azo compound.

> Dehydrothiotoluidine sulphonic acid — Beta-naphthol.

1889. Dark red powder, soluble in water. In concentrated H_2SO_4, red-violet solution ; on dilution, red ppt.

Application —An acid colour. Dyes *wool* and *silk* red from an acid bath.

CLAYTON COTTON BROWN (Cl. Co.). An azo dye.

> Dehydrothiotoluidine sulphonic acid
> Naphthylamine sulphonic acid
> > Phenylene diamine.

1890. Brown powder, soluble in water. In concentrated H_2SO_4, violet solution ; on dilution, chocolate ppt.

Application. — A direct cotton colour. Dyes unmordanted *cotton* brown from a salt bath.

CLAYTON WOOL BROWN (Cl. Co.). An azo compound.

> Aniline
> Sulphanilic acid —> Meta phenylene diamine.
> Naphthionic acid

1891. Brown powder, soluble in water.

Application.—An acid dye. *Wool* and *silk* brown from an acid bath.

CLAYTON YELLOW (Cl. Co.) *v.* THIAZOL YELLOW.

CLEMATINE (G.). *Safranine M N* (B.). A safranine colour. *Dimethyl tolusafranine chloride.* Metallic-looking powder, giving a red-violet aqueous solution. In concentrated H_2SO_4, green, becoming blue, then violet on dilution.

Application.—A basic colour. Dyes *wool* or tannin-mordanted *cotton* reddish-violet. Used also in *calico* printing.

CLOTH BROWN RED SHADE (By.) (L.). An azo compound.

> Benzidine
> > Salicylic acid.
> > Alpha-naphthol sulphonic acid N W.

1887. Dark reddish-brown powder, soluble in water. In concentrated H_2SO_4, blue-violet solution ; on dilution, red-brown ppt.

Application.—An acid colour. Dyes *wool* brown-red from an acid bath. The colour is much faster to milling if dyed upon, or fixed after dyeing with, chrome mordant.

CLOTH BROWN YELLOW SHADE (By.) (L.). An azo dye.

> Benzidine
> > Salicylic acid.
> > (2 : 7) Dioxynaphthalene.

1887. Dark brown powder, soluble in water. In concentrated H_2SO_4, reddish-violet solution ; on dilution, brown ppt.

Application. — *v.* CLOTH BROWN RED SHADE.

CLOTH ORANGE (By.) (L.). An azo dye.

> Benzidine
> > Salicylic acid.
> > Resorcinol.

1887. Red-brown powder, giving yellowish-brown solution in water. In concentrated H_2SO_4, red-violet solution ; brown ppt. on dilution.

---

* *Chemical News*, vol. lxvi., p. 169.
† *Ibid.*, vol. xxxi., p. 277.

Application. — *v.* Cloth Brown Red Shade. Gives brownish-orange colour.

CLOTH RED B (By.) (D.). An azo compound.

$$Amido\ azotoluol\ —\ \begin{array}{c}Alpha\text{-}naphthol\ sul\text{-}\\phonic\ acid\ N\ W.\end{array}$$

1879. Dark reddish-brown powder, soluble in water. In concentrated H_2SO_4, black-blue solution ; on dilution, bluish-red.

Application. — *v.* Cloth Brown Red Shade.

CLOTH RED B (O.). *Cloth red O* (M.), *Cloth red B A* (Ber.), *Fast bordeaux O* (M.). An azo compound.

$$Amido\ azotoluol\ —\ \begin{array}{c}Beta\text{-}naphthol\ disul\text{-}\\phonic\ acid\ R.\end{array}$$

1879. Dark brown powder, giving a magenta-red solution in water. In concentrated H_2SO_4, blue solution ; on dilution, brownish-red ppt.

Application. — *v.* Cloth Brown Red Shade.

CLOTH RED 3 B EXTRA (By.). An azo compound.

$$Amido\ azotoluol\ —\ \begin{array}{c}Ethylated\ beta\text{-}naphthyl\text{-}\\amine\ beta\text{-}sulphonic\ acid.\end{array}$$

1886. Dark brown powder, giving cherry-red aqueous solution. In concentrated H_2SO_4, green-blue solution, becoming dirty grey on dilution.

Application. — *v.* Cloth Brown Red Shade.

CLOTH RED G (By.). *Cloth red R* (D.), *Fast red 7 B* (N.J.). An azo compound.

$$Amido\ azobenzol\ —\ \begin{array}{c}Alpha\text{-}naphthol\ sulphonic\\acid\ N\ W.\end{array}$$

1883. Brown powder, giving magenta-red solution in water. In concentrated H_2SO_4, blue-violet solution ; on dilution, brownish-red ppt.

Application.—An acid dye. Dyes *wool* in acid bath red.

CLOTH RED G (O.). *Cloth red G extra* (By.), *Cloth red G A* (Ber.). An azo compound.

$$Amido\ azotoluol\ —\ \begin{array}{c}Beta\text{-}naphthol\ sulphonic\\acid\ S.\end{array}$$

1879. Reddish-brown powder, giving brownish-red solution in water. In concentrated H_2SO_4, blue solution ; on dilution, brownish-red ppt.

Application. — *v.* Cloth Brown Red Shade.

CLOTH RED 3 G EXTRA (By.). *Cloth red 3 G A* (Ber.). An azo compound.

$$Amido\ azotoluol\ —\ \begin{array}{c}Beta\text{-}naphthylamine\\sulphonic\ acid\ Br.\end{array}$$

Brown-red powder, giving red solution in water. In concentrated H_2SO_4, dark greenish-blue solution ; on dilution, brownish-red ppt.

Application. — *v.* Cloth Brown Red Shade.

CLOTH RED O (M.) *v.* Cloth Red B (O).

CLOTH RED R (D.) *v.* Cloth Red G (By.).

CLOTH SCARLET G (K.). An azo compound.

$$Amido\ azobenzol\ sulphonic\ acid\ —\ Beta\text{-}naphthol.$$

1878. Red-brown crystalline powder, giving red aqueous solution. In concentrated H_2SO_4, green solution, becoming blue, then red, and finally scarlet on dilution.

Application.—An acid colour. Dyes unmordanted or chromed *wool* red from an acid bath.

CLOTH SCARLET R (K.). An azo compound.

$$Amido\ azotoluol\ sulphonic\ acid\ —\ Beta\text{-}naphthol.$$

Dark brown paste, giving red solution in water. In concentrated H_2SO_4, green solution, becoming blue, then red, on dilution.

Application.—*v.* Cloth Scarlet G.

COAL. The chief kinds of coal are (1) *brown coal* or *lignite*, (2) *bituminous coal*, (3) *anthracite*. *Bituminous coals* are divided for commercial purposes into (1) *dry* or *free burning coals*, and (2) *caking coals*. When *dry coals* are heated they split up into plates, but *caking coals* swell up and soften when heated. *Cannel coal* is a variety of bituminous coal, which is valuable for producing illuminating gas. *Anthracite* is hard and brittle, and burns with a smokeless flame.

Coal varies considerably in composition. The amount of *ash* varies from 2·0 to 68   %

,,	*sulphur*	,,	0·2 ,,	10 ,,
,,	*oxygen*	,,	0·5 ,,	15 ,,
,,	*nitrogen*	,,	0·5 ,,	2·5 ,,

Phosphorus and *sulphur* are to be avoided as much as possible in coal. The *ash* and *oxygen* are also useless for heating purposes.

In taking samples of coal it is essential to obtain portions from each part of the bulk, and carefully take from these a smaller sample. The *sulphur* in coal exists chiefly as *iron pyrites*, FeS_2, commonly known as "brasses" when occurring in lumps. Sulphur is also present as *calcium sulphate*, and in combination with organic matter. During combustion, about three-fourths of the sulphur remains in the ash.

Analysis—Moisture.—2 grms. of the finely powdered sample are weighed between watch glasses, and heated for one hour at 105° C. The loss is reckoned as moisture.

Ash is estimated by carefully burning 3 grms. of coal in a platinum basin. The ash must be heated either over a Bunsen burner or in a muffle until free from carbon and of constant weight.

Total sulphur may be determined by the method employed by Hundeshagen. 2 grms.

of coal are mixed with 1·5 grms. of pure dry potassium carbonate and 3 grms. of magnesium oxide, and placed in a platinum crucible, a mixture of 0·5 grm. K_2CO_3 and 1 grm. MgO being spread over the mixture. The crucible is then heated to redness for half an hour, care being taken to prevent access of sulphur compounds from the gas burner. When cold, the mass is boiled out with water and dilute hydrochloric acid, and evaporated to dryness. The basin is heated to 130° C. to cause the silica to become insoluble, taken up with hydrochloric acid, diluted with hot water, and filtered. The filtrates which should occupy a volume of at least 200 c.c., is boiled and treated with hot solution of barium chloride. The precipitated barium sulphate is treated as on p. 12.

Nitrogen is estimated by heating the coal with soda lime and collecting the ammonia evolved in excess of standard acid and titrating with standard soda solution.

Volatile Matter and Coke.—1 grm. of ground coal is heated in a covered platinum crucible over a good Bunsen burner for two minutes, and immediately after for two minutes over a blowpipe flame. When cold the crucible and its contents are weighed. The loss = *volatile matter + water.* The residue = *coke + ash.*

The calorific power may be determined by means of Thompson's calorimeter. 2 grms. of dried coal or coke are mixed with 21 grms. of previously dried and powdered potassium chlorate and 7 grms. of potassium nitrate. The whole mixture is placed in the cylinder supplied with the apparatus. A small piece of cotton wick which has been saturated with potassium nitrate and dried is attached as a fuse. The cylinder is placed in the condenser (a copper cylinder furnished with clutches), and the whole apparatus immersed in 2000 c.c. of water in the glass vessel. The temperature of the water is read off, the apparatus withdrawn from the water, the condenser is removed and the fuse lighted. After quickly replacing the cylinder in the clamps the whole is again lowered into the water. The combustion takes place quickly, and when no more gas escapes from the holes in the condenser the stopcock is opened and the apparatus moved up and down in the water until the temperature is constant. The thermometer is then carefully observed, and the height of the mercury column is noted.

Example.—

Temp. of water before experiment, 15·5° C.
  ,,   ,, after   ,,   22·8° C.
Rise of temperature . = 7·30° C.
Absorption of heat by calorimeter $\frac{1}{10}$, ... ·73° C.
                —————
                8·03° C.

H. J. Phillips in his *Engineering Chemistry* finds from experiments which he has made on the amount of coal which escapes combustion by the above method that a correction of 0·21° C. from the figures obtained represents the heat lost by this unburnt coal.

Hence the more correct result is 8·03 − 0·21 = 8·24.

$$8·24 \times 1000 = 8240 \text{ calories.}$$

∴ 1 lb. of this sample of coal raises the temperature of 6360 lbs. of water 1° C.

The *evaporating power* of this coal—that is, the amount of water in lbs. evaporated at 212° F. (100° C.) by 1 lb. of the sample—is

$$\frac{8240}{537} = 15·3.$$

(The figure 537 is the latent heat of steam.)

COAL-TAR COLOURS.

ORIGIN.

During the dry distillation of coal for the manufacture of illuminating gas, certain volatile products are evolved which subsequently condense and separate into two portions—a watery liquid, and a thick tarry mass. The former is the chief source of ammonia and ammonium salts, the latter constitutes *coal-tar.*

By distillation and chemical treatment various products are obtained from coal-tar, and the following are those of chief importance in the colour industry :—*Benzene* (C_6H_6), *Phenol* ($C_6H_5 . OH$), *Naphthalene* ($C_{10}H_8$), *Anthracene* ($C_{14}H_{10}$). Each of these substances is the basis of the manufacture of a large series of dyes.

CLASSIFICATION.

There are at the present time about 2000 distinct coal-tar colours offered for practical use, and they may be classified—

I. According to their Source of Origin.— This method of grouping distinguishes (*a*) *Aniline dyes* or benzene derivatives, (*b*) *Naphthalene dyes*, (*c*) *Anthracene dyes*, (*d*) *Derivatives of phenol*, &c., but since many dyes contain more than one of the above substances— some, for instance, containing both naphthalene and phenol groups—this classification is useless.

II. According to Chemical Constitution. —The constitution of a dyestuff greatly influences its dyeing properties and its behaviour under various conditions, but this statement must not be pushed too far, since similarly constituted dyes have in many cases different properties.

In classifying dyes according to chemical constitution, the following principal groups may be distinguished * :—

* Following Schultz and Julius's *Tabellarische übericht der künstlichen Farbstoffe.*

Class.	Characteristic Group or Chromophor.
1. Nitro compounds, ...	$-NO_2$
2. Azoxy compounds, . . .	$-N-N$ over O
3. Azo compounds, ...	$-N=N-$
4. Triphenylmethane derivatives,	$C \begin{cases} C_6H_5 \\ C_6H_5 \\ C_6H_5 \\ H \end{cases}$
5. Pyronine derivatives, . . .	(ring) O ... C
6. Acridine derivatives, . . .	(ring) N ... C
7. Nitroso compounds, . . .	$N(OH)$, O (ortho)
8. Oxyketone derivatives,	CO and two (OH), the latter in ortho position as regards each other.

Class.	Characteristic Group or Chromophor.
9. Oxazines and	O (ring) N
Thiazines, ...	S (ring) N
10. Azine dyes, . . .	N (ring) N or N (ring) N
11. Thiobenzenyl derivatives,	$\begin{matrix} S \\ N \end{matrix}$ (ring) $C-$

III. Classification according to Method of Application.—This grouping is the most valuable from the point of view of the practical dyer, and the following are the chief divisions recognised :—

1. Acid colours.
2. Basic dyes.
3. Direct cotton dyes.
4. Mordant dyes.
5. Acid mordant dyes.
6. Dyes applied by oxidation, reduction, or other special processes.

In the description of the various coal-tar colours given in this work, the names of the firms by whom the particular dye treated of is manufactured is indicated by contractions, to which the following list is an explanatory reference :—

CONTRACTION.	FIRM REFERRED TO.
B. or B.A.S.F., . .	Baden Aniline Co., or Badische Anilin und Soda-Fabrik, Ludwigshafen-on-Rhine.
B.A. Co., ...	British Alizarin Co., London.
Ber. or Berlin, . .	Berlin Aniline Co., or Actien-Gesellschaft für Anilin Fabrikation, Berlin.
By. or Bayer, . . .	The Bayer Co., or Farbenfabriken vorm. Fr. Bayer & Co., Elberfeld.
B.K., ...	Beyer & Kegel, Leipzig.
Br.S. or Br.S. & S., . .	Brook, Simpson & Spiller, Ltd., London.
C. or Cassella, . .	L. Cassella & Co., Frankfurt.
Cl. Co. or Clayton, . .	Clayton Aniline Co., Manchester.
C.R., ...	Claus & Rée, Manchester.
D. or Dahl, . . .	Dahl & Co., Barmen.
D. & H. or Durand, . .	Durand, Huguenin & Co., Basle.
Fi. or Fischesser, . .	A. Fischesser & Co., Mulhausen.
G. or Geigy, . . .	J. R. Geigy, Basle.
H. or Holliday. . .	Read Holliday & Sons, Ltd., Huddersfield.
K. or Kalle, . . .	Kalle & Co., Biebrich.
L. or Leonhardt, . .	Leonhardt & Co., Mühlheim.
Lev. or Levinstein, . .	I. Levinstein & Co., Ltd., Manchester.
M. or M.L. & B., . .	Meister, Lucius & Brüning, Höchst.
Mo. or Monnet, . .	Gilliard, Monnet & Cartier, Lyons.
O. or Oehler, . .	K. Oehler, Offenbach.
P. or Poirrier, . . .	Société Anonyme des Matières Colorantes (A. Poirrier and G. Alsace), St. Denis.
S.C.I. or Bindschædler, .	Society of Chemical Industry (Bindschædler & Busch), Basle.
Sch. or Schollkopf, . .	Schollkopf Aniline Co., Buffalo.

ANALYSIS AND VALUATION OF COAL-TAR COLOURS.

With few exceptions, the coal-tar colours as a class can only be satisfactorily valued by means of experimental dye trials. The exact mode of procedure varies according to the properties of the colouring matter and the purposes to which it is to be applied. In conducting these dye trials a given weight of colouring matter (about 1 grm.), whenever possible, should be dissolved in a litre of water and an aliquot part taken, corresponding to, in the case of pure colouring matter, from 0·2 to 0·5 per cent., but in the case of paste dyes, such as alizarins, from 2 to 5 per cent. will be required. The results of comparative dye trials are only of value when the conditions in each case are identical, or as nearly so as possible. When comparatively small quantities of colouring matter are used, wool and silk, in the majority of cases, leave but little colour in the bath. In some cases, however—with alkali blue, for example—a large proportion of colour is left in the bath. In making comparative tests of such dyes, a second lot of material should always be dyed without any further addition. In many cases colorimetric tests afford much useful information. The observations serve either as a preliminary to making dye tests or as a confirmation of them. Colorimetric tests are not of much value unless the dyes under examination are of the *same kind* and of a *similar shade*. Methods of making these tests are given under colorimetry. There are very few published methods for determining the value of colouring matters other than by experimental dye tests.

In the *Journal of the Society of Dyers and Colourists* (1888, p. 82), Rawson describes a method for determining the value of naphthol yellow and certain other coal-tar colours. The principle of the process might be applied in numerous other cases. Naphthol yellow S occurs in the market under various names and in various degrees of strength. Some qualities are practically pure, whilst others contain more or less sulphate or chloride of sodium. The method employed for determining the tinctorial value depends upon naphthol yellow forming an insoluble precipitate with a solution of night blue (tetramethyltolyltriamido-diphenylnaphthylcarbinol hydrochloride). A *standard solution of night blue* is prepared by dissolving 10 grms. in 50 c.c. of glacial acetic acid, and diluting with water to a litre. Solutions of the samples of naphthol yellow S are prepared so as to contain 1 grm. per litre. The operation is carried out as follows :—10 c.c. of night blue solution are carefully measured into a small flask and then about 30 c.c. of the yellow run in from a burette ;

the mixture is well shaken for about 1 minute, and is then run on to a filter. If the filtrate be of a distinct yellow colour, a second experiment is performed in a similar manner with a smaller quantity of the solution of yellow. If the filtrate be blue, or even colourless, more of the yellow solution is required. These experiments are repeated with various quantities of the naphthol yellow solutions until the filtrate possesses a faint, scarcely perceptible yellow tint. It is best to collect the filtrate in clear Nessler glasses. With a little practice the number of experiments may be reduced to three or four. The value of the samples under examination will be in inverse proportion to the number of cubic centimetres required to precipitate 10 c.c. of night blue. For example, if of two samples one requires 28 c.c. and the other 35 c.c., their relative value will be as 35 : 28, or, expressed centesimally, as 100 : 80. If it be desired to express the percentage of pure colouring matter present in the samples, the night blue may be standarised by means of re-crystallised naphthol yellow S, which is the potassium salt of dinitro-α-naphthol sulphonic acid. 1 grm. of commercial night blue precipitates about 0·25 grm. of pure, dry naphthol yellow S. It would thus appear that 2 molecules of night blue combine with 1 molecule of naphthol yellow S to form the insoluble precipitate. The method is applicable to the valuation of the azo dyes, but in such cases it must be used with discretion. Colouring matters which are to be compared with one another must possess a *similar constitution*. It would not be correct, for example, to compare a croceïn scarlet with a xylidine scarlet. But a number of samples of either of the scarlets, containing various proportions of either mineral or organic adulterations, can be valued by the night blue process with great precision. P. Kay and J. R. Appleyard have applied the process to the valuation of picric acid. They also found that crystal violet (hexamethylrosaniline hydrochloride) gave a similar insoluble precipitate with picric acid. Kay further shows that picric acid may be estimated by a solution of caustic potash, using phenolphthaleïn as indicator. Of course the method is only applicable in the absence of acid or alkaline salts. Some coal-tar colours may be estimated by means of a standard solution of sodium hyposulphite in a similar manner to that described for indigo. The operation must be conducted in a closed vessel, from which the air has been expelled by a current of CO_2, and since the decolorisation only takes place at 100° C., the liquid under examination must be raised to the boiling point. 1 molecule of a dye, such as magenta, Hofmann's violet, &c., requires for complete decolorisation the same quantity of hyposulphite as that which is required to

reduce 2 molecules of ammoniacal copper sulphate. Whatever means are adopted to determine the amount of colouring matter present in commercial dyes, practical dye tests will always be required to ascertain the shades which they are capable of producing on the textile fabrics.

Impurities.—Some of the commercial artificial dyes consist of practically pure colouring matter, many others contain more or less impurities of manufacture, and a numerous class contain mineral salts as well as organic substances purposely added. Sodium chloride, sodium sulphate, and dextrin are the most common substances present, but sodium carbonate, magnesium, potassium, and ammonium salts may occasionally be found. The presence of any of these bodies in an artificial dye does not necessarily indicate adulteration, unless, of course, the product is represented as a pure colouring matter. In many cases the pure colouring matter cannot be conveniently prepared on a commercial scale, and as the manufactured product is liable to vary in strength, it is reduced to a given standard by some inert substance. *Sodium sulphate* is used largely for azo dyes, *dextrin* and *common salt* for basic dyes. *Sulphates* may usually be detected by adding hydrochloric acid and barium chloride to a dilute solution of the dye. In some cases it is preferable to precipitate the colouring matter by *pure* sodium chloride, and test the filtrate as above. Alkaline salts of sulphonated dyes leave, on ignition, alkaline sulphates, so that the presence of a sulphate in the ash does not indicate the presence of sodium sulphate in the colouring matter. *In the absence of sulphates,* the detection of sulphuric acid in the ash indicates the presence of a sulphonic acid group or groups in the colour.

Chlorides in many cases may be detected by simply adding nitric acid and silver nitrate to a dilute solution of the dye. If the colouring matter is soluble in strong alcohol it should be extracted by warming with that solvent, and the residue tested for common salt.

Dextrin may generally be recognised by its smell when the dye is dissolved in warm water, also by its insolubility in alcohol. When it has been mixed in the dry state (which is usually the case), it is best detected by means of the microscope ; unconverted starch being always present in the dextrin.

Mixed Dyes.—Many of the dyes found in commerce, sold under various names, are mixtures of two or more colouring matters. When the dyes have been *mixed in the powdered state,* they may be recognised in the following manner :—A filter paper is moistened with water or alcohol, and a little of the powdered dye is gently blown on to it. Each particle slowly dissolves, forming a little spot or streak, and if more than one colouring matter is present it is readily detected. Mixtures of many of the azo dyes are more easily recognised by blowing a little of the powdered substance over the surface of concentrated sulphuric acid contained in a porcelain basin. When the colouring matters have been *mixed in solution and evaporated* together, the above tests are not reliable. In such cases, successive lots of wool, silk, or cotton are dyed in a solution of the sample, and the shade compared. The dyed swatches are dried, and small pieces tested with various reagents. If the sample was a mixture, the first swatch dyed will probably show different reactions to the last. Mixtures of dyes may also be detected by *capillary analysis.* The following abstract of a paper by Goppelsrœder on this subject is taken from the *Journal of the Society of Dyers and Colourists,* 1888, p. 5 :—

Based upon some experimental researches by Schönbein in 1862, which showed that different substances when dissolved in water have a different velocity of propagation by capillary attraction in porous material, such as unsized paper, Goppelsrœder has examined in particular the behaviour of colouring matters in this respect. The colouring matters, or mixtures of them, were, if possible, dissolved in water or alcohol, or, if these liquids proved ineffective, in some other solvent which had no chemical action. The porous medium employed was pure (Swedish) white filtering paper cut into strips of different breadth and length, according to the quality and complexity of the (not concentrated) colour solution under examination. A number of such strips of paper were suspended at one end, while 5 to 10 millimetres of the other end were made to dip into the solution contained in a series of glasses. The time of immersion was usually fifteen minutes. By the action of capillary attraction, the water contained in the solution begins to rise in the paper, reaching a greater height in a given time than all other substances. Picric acid stands next in the velocity of rising, and by dipping a strip of filtering paper in an aqueous solution containing picric acid and turmeric the different zones will appear after a given time—a highest narrow zone containing water, a middle broad zone of yellow picric acid, and a third and lowest zone of the appearance of the yellow colouring matter of turmeric. By immersing the strip of paper into a dilute solution of potash the zone of picric acid disappears, while the zone with the turmeric turns brown. A single operation is therefore sufficient for nearly complete separation of the two colouring matters. If now the lowest zone of turmeric yellow is cut off, and the colouring matter in it dissolved in alcohol, a repetition of the operation will again produce three zones— the highest containing alcohol, the middle zone a few lines in breadth, and coloured a very faint yellow with the picric acid. The turmeric zone turns brown in gaseous ammonia, while the zone of picric acid remains unaltered ; in a weak alkaline solution the latter is decolorised, the picric acid being dissolved. By operating upon a mixture of an aqueous solution of picric acid and one of indigo extract, four zones were obtained when the solution had a purely green colour without prevalence of blue or yellow—a lowest broad zone of a greenish colour, above it a second much narrower zone of pure yellow, above this a third zone containing sulphuric acid, a fourth zone containing pure water, a drop of tincture of litmus not turning red when applied to it. Two zones only were obtained from a mixture of a little picric acid

with much indigo extract—a lowest broad zone of an intense bluish-green, a middle purely yellow zone, and a highest zone of sulphuric acid, no water being separated in this case. In commercial magenta, prepared by the action of arsenic acid on aniline oil, traces, at least, of a yellow colouring matter could always be distinctly detected by capillary analysis. But if the filter paper is dipped a few millimetres into an alcoholic solution of a well crystallised salt of rosaniline, four zones are observed after a few moments—a highest colourless zone of pure alcohol, and three others of a light pink, pink, and deep red in succession. An addition of a trace only of picric acid produces (1) a pink and deep red coloured zone, (2) a colourless zone, (3) a narrow zone of picric yellow. The more picric acid was added to the magenta the broader was the yellow zone of picric acid and the narrower the brownish-red zone of magenta. Samples of commercial magenta produced, besides the red zone, a more or less broad yellow zone, which appears most distinct if the alcoholic solutions of magenta are employed in a very concentrated state, and if the filter paper is immersed long enough for the deposition on it of the magenta with a dark brownish-red colour.

RECOGNITION OF COAL-TAR DYES.

Witt,[*] in 1886, proposed the first definite scheme for the determination of coal-tar dyes, separating them into groups according to their colour, solubility, and behaviour with caustic soda.

Weingärtner,[†] in 1887, published a much more extended scheme, classifying the dyes into "acid" or "basic," according to their reaction with tannic acid; and into smaller groups by their behaviour upon reduction with zinc dust.

Taking Weingärtner's scheme as a basis, A. G. Green[‡] has worked out a much more satisfactory process, by means of which a very large number of dyes may be identified. The main reactions made use of are—

1. Solubility or insolubility in water.
2. Precipitation or non-precipitation by tannic acid.
3. Reduction by zinc dust with subsequent re-oxidation.

In the application of the zinc dust reaction Green found that whilst the derivatives of *triphenylmethane* after reduction are re-oxidised by air only with great difficulty, the *azines*, *oxazines*, *thiazines*, and *acridine* colours all re-appear with great rapidity on exposure of the reduced solutions to the atmosphere. He accordingly makes use of this difference of behaviour, which is very marked, to differentiate these two groups of colours. On the other hand, the triphenylmethane colours are distinguished from those which do not yield leuco compounds, but are completely broken up on reduction by the colour of the reduced solution being restored

by chromic acid. The *quinoline* and *primuline* colours are distinguished from other dyestuffs by the great difficulty with which they are reduced—primuline, for instance, remaining unaltered after long boiling with zinc dust and ammonia.

The analytical scheme which is based upon these reactions is contained in the annexed tables (p. 98, *et seq.*).

The reduction with zinc dust requires to be performed with some care. It is usually best to add a little zinc dust to the hot solution of the colouring matter contained in a test tube, agitate, and then add dilute hydrochloric acid drop by drop until decolorised. An excess of acid must be carefully avoided. In other cases, more especially when the colour acid is very insoluble, the reduction must be performed with zinc dust and ammonia; but it is usually safest to repeat the tests with both methods of reduction.

Whilst it is important that the colouring matter should be completely reduced, care should also be taken that the reduction is not carried too far, for some colouring matters (*e.g.*, *indulines*) which usually form oxidisable leuco compounds are thereby completely altered. When reduced the solution is poured off from the greater part of the zinc dust on to a piece of white filter paper and exposed to the air; filtration is unnecessary, as a little zinc upon the paper has no injurious effect. If the colour does not return in a minute or two, the paper is touched with a glass rod dipped in a 1 per cent. solution of chromic acid (with addition of sulphuric acid for acid colours). Warming gently for a few seconds over a flame facilitates the reactions, and should also be employed when the reduction has been performed with zinc dust and ammonia, in order to remove the excess of the latter before adding chromic acid, which would otherwise be neutralised.

In the case of acid colouring matters, the paper, after spotting with chromic acid, should be held over a bottle of strong ammonia, for some acid colours (*e. g.*, the *eosines*) do not show their true colour whilst acid. On reduction of those eosines which contain iodine, a brown spot of the latter is obtained with chromic acid, but this disappears on exposure to ammonia vapour, and the original colour of eosine (or a rather yellower shade) returns. As already pointed out by Weingärtner, great care must be taken that one is not led astray by secondary colours formed by oxidation of the diamines and amidophenols obtained by reduction of azo colours.

A. G. Rota[*] has developed a method for the recognition of coal-tar dyes, chiefly based on their behaviour on reduction in very dilute

* *Chem. Ind.*, vol. ix., p. 1. Abstracted in *Journ. Soc. Chem. Ind.*, 1886, p. 249.
† *Chem. Zeit.*, 1887, p. 135. Abstracted in *Journ. Soc. Dyers and Col.*, 1887, p. 66.
‡ *Journ. Soc. Chem. Ind.*, 1893.

* *Chem. Zeit.*, 1898, pp. 437-442. Abstracted in *Journ. Soc. Chem. Ind.*, 1898, pp. 210-214.

ANALYTICAL SCHEME.

Group Reagents.—
1. A solution containing 10 per cent. of tannin and 10 per cent. of sodium acetate.
2. Zinc dust and dilute hydrochloric acid, or zinc dust and aqueous ammonia.
3. Solution containing 1 per cent. of chromic acid (for basic colours).
4. Solution containing 1 per cent. of chromic acid or potassium bichromate and 5 per cent. of sulphuric acid (for acid colours).

Distinguishing Reagents.—The members of the same group are distinguished from each other by their behaviour towards aqueous acids and alkalies, concentrated sulphuric acid, alcohol, &c., and by their dyeing properties. See the reactions of the various colours as given by Witt, Weingärtner, and others.

GROUP I.—DYESTUFFS SOLUBLE IN WATER.

A.—Precipitated by Tannin Solution: Basic Colours.

The aqueous solution is reduced with zinc dust and hydrochloric acid and a drop of the decolorised solution put on filter paper. If the colour does not quickly return on exposure to air, the spot is touched with a drop of 1 per cent. chromic acid solution.

The original colour quickly re-appears on exposure to air: Azine, Oxazine, Thiazine, and Acridine Colours.					The colour re-appears very slowly or not at all on exposure to air, but returns on spotting with 1 per cent. chromic acid solution: Triphenylmethane Colours, and Basic Phthaleïns.				The original colour does not return at all.
Red.	Orange and Yellow.	Green.	Blue.	Violet.	Red.	Green.	Blue.	Violet.	Yellow and Brown.
Toluylene Red. Safranine.	Phosphine. Benzoflavine.	Azine Green.	Methylene Blue. New Methylene Blue N.	Mauve. Amethyst.	Magenta. Isorubine.	Malachite Green. Brilliant Green.	Victoria Blue B. * Victoria Blue 4 R.	Methyl Violet. Crystal Violet.	Auramine.‡ Thioflavine T.§
Pyronine. Acridine Red.	Acridine Yellow. Acridine Orange.		Thionine Blue. Toluidine Blue.	Neutral Violet. Fast Neutral Violet.	†Rhodamine.	Methyl Green. Iodine Green.	Night Blue.	Hofmann Violets. Benzyl Violet.	Chrysoïdine. Bismarck Brown.
			Meldola's Blue. Muscarine.	Prune. Paraphenylene Violet.				Ethyl Purple. Regina Purple.	
			Neutral Blue. Basic Blue R and B B.	Indamines.					
			New Methylene Blue G G.						
			Nile Blue. Capri Blue. Fast Black. Indazine M. Metaphenylene Blue B. Paraphenylene Blue. Indamines.						

* The shade which returns is much greener than the original.　　　† The colour returns more quickly than with the rosanilines.
† The reduced solution gives a beautiful violet when the spot on filter paper is warmed over a flame till dry.　　§ Is only reduced with difficulty and very slowly.

ANALYTICAL SCHEME—Continued.

B.—Not Precipitated by Tannin Solution: Acid Colours.

The aqueous solution is reduced with zinc dust and hydrochloric acid, or with zinc dust and ammonia, and a drop of the decolorised solution is put on filter paper. If the colour does not quickly return on exposure to air, the spot is touched with a drop of chromic acid solution (1 per cent. CrO_3 + 5 per cent. H_2SO_4), warmed over a flame, and then held in the vapour of ammonia.

The solution is decolorised.							Not decolorised (by zinc and ammonia), but changed to brownish-red. Original colour returns quickly on exposure to air.	Very slowly and incompletely decolorised (zinc and ammonia).	Not altered by zinc and ammonia; very slowly or not at all by zinc and hydrochloric acid.
The original colour quickly re-appears on exposure to air.	The original colour does not re-appear on exposure to air, or only very slowly, but returns with chromic acid, and exposure to ammonia vapour.	The aqueous solution of the dyestuff is acidified and shaken with ether.		The original colour does not return at all: Azo, Nitro, Nitroso, and Hydrazine Colours.					
Sulphonated azines, oxazines, thiazines, &c.:—		The ether extracts the colour-acid, leaving the solution nearly colourless: — Phthaleïnes and Aurines:—	The ether remains colourless: — Sulphonated triphenylmethane colours:—	Heated on platinum foil. Deflagrates with production of coloured vapours: — Nitro-colours:—	Heated on platinum foil. Burns quietly or deflagrates slightly, giving off coloured vapours:—Azo, nitroso and hydrazine colours. The colour dyed upon unmordanted cotton. Resists warm soap. — Substantive Azo colours.	The colour dyed upon unmordanted cotton. Is stripped by warm soap. — Ordinary Azo colours.			
Soluble Indulines.†	Resorcin Blue.	Uranine.	Acid Magenta.	Picric Acid.		Naphthol Green B.	Alizarin S.	Clayton Yellow.	Quinoline Yellow S
Soluble Nigrosines.†	Azurine.	Chrysoline.	Acid Violets.	Victoria Yellow.		Tartrazine.	Alizarin Blue S.	Thiazol Yellow.	Primuline.
	Thiocarmine.	Eosine.	Formyl Violet.	Aurantia.			Cerulin S.	Turmerine.	Thioflavine S.
	Basle Blue R S and B B S.	Erythrine.	Alkali Blues.	Martius Yellow.				Mimosa.	Oxyphenine.
	Gallamine Blue.	Phloxine.	Soluble Blues.	Naphthol Yellow S.					
	Gallocyanine.	Erythrosine.*	Patent Blue.	Brilliant Yellow.					
	Gallanilic Indigo P S.	Rose Bengale.*	Fast Green, bluish.	Aurotine.					
	Indigo-carmine.	Cyclamine.*	Acid Greens.						
	Saffrosine.	Aurine.	Guinea Green.						
	Azo-carmine.	Coralline.	Chrome Violet.						
	Mikado Orange.†								

* Iodine is separated by the chromic acid, but disappears on exposure to ammonia.

† If the reduction is carried too far, the colour does not return.

ANALYTICAL SCHEME—Continued.

Group II.—Dyestuffs Insoluble in Water.

The powder or paste is treated with water and a few drops of 5 per cent. caustic soda solution.

The colour dissolves.		The colour remains insoluble.			
The alkaline solution is heated with zinc dust and ammonia, and a drop is put on filter paper.		Soluble in 70 per cent. alcohol.			Insoluble in 70 per cent. alcohol.
Decolorised or changed to light-brown. The original colour returns very quickly on exposure to air.	Decolorised or changed to brown. The original colour does not re-appear on exposure to air.	Solution not fluorescent.		Solution fluorescent.	Indigo. Aniline Black. Primuline Base.
		On adding caustic soda (33 per cent.) to the alcoholic solution.		On adding caustic soda (33 per cent.) to the alcoholic solution.	
		Colour becomes reddish-brown.	Colour not altered.	Fluorescence destroyed.	Fluorescence remains.
Coerulein. Gallein. Gallocyanine. Gallanilic Violet B S. Gallanilic Blue P. Galloflavin. Alizarin Blue. Alizarin Black. Alizarin Cyanine. Alizarin Cyanine Black. Rufigallol.	Alizarin. Anthrapurpurin. Flavopurpurin. Alizarin Orange. Alizarin Brown. Alizarin Bordeaux. Alizarin Yellow G G & R. Chrysamine. Sudan Brown. Patent Fustin. Myrtle or Russian Green. Gambine R and Y. Dioxine.	Induline, Opal. Nigrosine, Opal. Rosaniline Blue, Opal. Diphenylamine Blue, Opal.	Indophenol. Sudan II. and III. Carminaphth.	Magdala Red.	Spirit Eosines. Cyanosine.

solution (1 in 10,000). The aqueous or alcoholic solution is diluted to about 1 : 10,000, and 5 c.c. of this are treated with 4 to 5 drops of concentrated hydrochloric acid and the same quantity of a 10 per cent. stannous chloride solution obtained by dissolving tin in hydrochloric acid. The mixture is shaken and if necessary heated to boiling. If the solution does not decolorise entirely, the dyestuff is to be still further diluted or a further quantity of stannous chloride added. Accepting Armstrong and Nietzki's quinone theory, it would appear that under certain conditions stannous chloride reduces those dyestuffs which can be referred to the mono- and di-imido types, whilst those in which one oxygen atom is replaced by a divalent carbon group are not reduced. Thus considering $O : R : O$ as an o- or p-quinone, dyestuffs belonging to the *nitro, nitroso, azo,* and *quinone imide* groups—*i.e.*, having the constitution $O : R : N$ (oxyquinoneimide), or $. N : R : N$ (quinone-di-imide), are reducible, whilst *oxyquinone* and *triphenylmethane* dyestuffs $O : R : C :$ (oxycarboquinone), and $. N : R : C :$ (imido-carboquinone), are not reduced. The reduced solution after neutralisation with potash lye is treated with a few drops of ferric chloride, or is shaken with air. Some solutions remain unchanged, whilst in others the dyestuff is regenerated. Belonging to the former are the nitro, nitroso, and azo dyestuffs which give stable amines on reductions, whereas the latter, the quinone imido derivatives, forming leuco derivatives, are easily oxidised. The non-reducible dyestuffs can be further divided into two classes, the oxy-carboquinone and the imidocarboquinone derivatives. The latter include the magentas, acridines, &c., which on treatment in hot aqueous solution with caustic potash lye are decolorised or precipitated, whilst the former, by virtue of their acid character, give coloured salts with alkalies usually easily soluble in water. Dyestuffs can thus be divided into four groups, to which two or three large subdivisions belong having similar chromophores, the differences depending upon the different salt forming groups *amido, imido, carboxyl,* or *sulphonic acid.* The detection of these is effected by ether or by means of suitable fibres, as will be shown later. The dyestuff is examined by the help of the following tables, by means of which it is assigned to the particular group or subdivision to which it belongs, and is then further identified by one of the published tables of dyestuffs. It is, however, to be borne in mind that these tables do not contain many of the dyestuffs now on the market. It may thus be necessary to examine the solution spectroscopically or to decompose the dyestuff into simpler or more easily recognisable components. For example, the various *phthaleïns*

TABLE A.—*Classification of Organic Dyestuffs.*

A portion of the aqueous or aqueous alcoholic solution of the dyestuff is treated with hydrochloric acid and then with stannous chloride solution.

The solution is decolorised.* Reducible Dyestuffs.		No further change than with hydrochloric acid alone. Non-reducible dyestuffs.	
The decolorised solution after neutralisation with potash lye or sodium acetate is oxidised with ferric chloride or atmospheric oxygen.		A portion of the original solution is treated with 20 per cent. potash lye, and warmed if necessary.	
No change. Non-oxidisable dyestuffs.	Original colour returns. Re-oxidisable dyestuffs.	Solution decolorised or a precipitate is formed. Imidocarboquinone dyestuffs.	No precipitate, the colour becomes more intense. Oxycarboquinone dyestuffs.
Group I. Nitroso, nitro, and azo dyestuffs, including azoxy and hydrazo colours.	Group II. Indogenide and quinone imide dyestuffs.	Group III. Amido derivatives of di- and triphenyl methane, auramines, acridines, quinolines, and thiobenzenyl dyestuffs.	Group IV. Non-amidated diphenyl methane dyestuffs, oxyketone dyestuffs (including most of the natural organic dyestuffs).

* Some indulines are only decolorised with difficulty, the solution never becoming quite colourless.

TABLE B.

Group I.—Dyestuffs Reducible with Stannous Chloride and Hydrochloric Acid, the Colour not Returning on Oxidation.

Nitro Dyestuffs, (R : NO₂).—Yellow or orange dyestuffs, soluble in water; dyeing wool and silk directly, but not cotton. The aqueous solution tends to decolorise with hydrochloric acid. On partial reduction with hydrochloric acid and stannous chloride, they give red nitro-amido derivatives (nitro-amines) or nitrophenols turning red in potash lye,

- Nitro-amines soluble in ether in presence of KOH, . . . } $N : R : N \diagdown OH$ (O) — e.g., Aurantia.
- Nitrophenols insoluble in ether in presence of KOH,
    - Unsulphonated, soluble in ether, in presence of acetic acid. } $O : R : N \diagdown H$ (O) — e.g., Victoria Yellow.
    - Sulphonated, in every case insoluble in ether, } Naphthol Yellow S.

Nitroso Dyestuffs, O : R : N . OH₂.—Brown or green, usually insoluble in water. Dye indirectly. Give a blue coloration with sulphuric acid and phenol (Liebermann's reaction),
- Unsulphonated, insoluble in alcohol, soluble in ether in presence of acetic acid, . . . } e.g., Dioxine.
- Sulphonated, soluble in water, insoluble in ether, . . . } e.g., Naphthol Green B.

Azo Dyestuffs, R . N : N . R.—Recognisable as not belonging to either of the two foregoing subdivisions. Their aqueous solution treated with potash lye and extracted with ether behaves as follows:—

- The solution is coloured, the colour being extracted by dilute acetic acid. *Basic dyestuffs,*
    - Unsulphonated amido-azo dyestuffs, . . . } $N : R : N . NHR'$ — e.g., Bismarck Brown.
    - Oxyazo dyestuffs not containing a carboxyl group, . . } $O : R : N . NHR'$ — e.g., Sudan I.

- Coloured solution. The colour is not extracted by dilute acetic acid. *Neutral dyestuffs,* *
    - Oxyazo dyestuffs with a carboxyl group,
        - Dye cotton indirectly — Diamond Yellow.
        - Dye cotton indirectly — Chrysamine.

- Colourless solution; acetic acid does not extract anything. *Acid dyestuffs,*
    - Unsulphonated, soluble in ether from dilute acetic acid,
        - Non-amidated, unchanged by HNO₂†,
            - Dye cotton directly — Bordeaux B.
            - Dye cotton directly — Azo Blue.
    - Sulphonated, insoluble in ether from dilute acetic acid,
        - Amidated, react with HNO₂,
            - Dye cotton indirectly — Fast Yellow N.
            - Dye cotton directly — Congo Red.

* Some amido-azo dyestuffs (Aniline Yellow) behave like neutral dyestuffs, but differ from these in being decolorised by nitrous acid.

† The presence of an amido group is detected by treating 5 c.c. of the warm solution with two to three drops of 1 per cent. dilute acetic acid and the same quantity of a 1 per cent. potassium nitrite solution. Amido derivatives are decolorised or the colour is modified, whilst non-amidated compounds remain unchanged or are not further affected than by acetic acid alone.

Table C.

Group II.—Dyestuffs Reducible with Stannous Chloride and Hydrochloric Acid, the Colour Returning on Oxidation.

The aqueous or alcoholic solution (5 c.c. of a strength 1 : 10,000) is treated with 4 to 5 drops of a 20 per cent. potash lye and extracted with 10 to 15 c.c. of ether. This solution washed with water (once with an equal volume if the original solution was aqueous, but two to three times if alcoholic), shows the following reactions :—

The solution is *coloured* or *colourless*, but imparts the original colour to 5 per cent. acetic acid when shaken with it. **Basic Dyestuffs.**— Dye wool from an alkaline bath.	The solution is easily reduced by hydrochloric acid and stannous chloride in the cold,	*Ozazines* (free from sulphur),	$N\left\langle{R' \atop R}\right\rangle O,\; R{=}N\equiv$	*, g.,* Meldola's Blue.
		Thiazines (contain sulphur),	$N\left\langle{R' \atop R}\right\rangle S,\; R{=}N\equiv$	*e.g.,* Methylene Blue.
	The solution is only difficulty reduced with difficulty and frequently imperfectly. It requires to be warmed, and an excess of hydrochloric acid and stannous chloride,	*Indulines.*—Blue colour with concentrated sulphuric acid, giving a blue solution on dilution with water,*	$N\left\langle{R' \atop R}\right\rangle N,\; R{=}N\equiv$	*e.g.,* Spirit-soluble Induline.
		Safranines.—Green colour with sulphuric acid, turning blue and then violet on dilution,	$N\left\langle{R \atop R}\right\rangle N:$	*e.g.,* Safranine T. extra.
Coloured.—The colour is not extracted by acetic acid. **Neutral Dyestuffs.**—Insoluble in water, soluble in alcohol; dye the fibre from an indigo vat.	Blue dyestuffs affected by warm hydrochloric acid,	*Indophenols,*	$N\left\langle{R \atop R}\right\rangle O$	*e.g.,* Indophenol.
	Red or blue dyestuffs unchanged by hydrochloric acid; give isatine with nitric acid,	*Indigenides,*	$HN\left\langle{R' \atop C:}\right\rangle CO$	*e.g.,* Indigotine.
Colourless, acetic acid does not extract anything. **Acid Dyestuffs.**—Soluble in water; dyeing wool from an acid bath.	*Unsulphonated.*—Soluble in ether in presence of acetic acid,	*Ozazones,*	$N\left\langle{R \atop R}\right\rangle O$	*e.g.,* Fluorescent Blue, Orcein.
	Sulphonated.— Not soluble in ether,	Easily reduced by stannous chloride and hydrochloric acid,	*Sulphonated Indogenides. Sulphonated Thiazines.*	*e.g.,* Indigo-carmine. *e.g.,* Thiocarmine R.
		Reduced with difficulty by stannous chloride and hydrochloric acid,	*Sulphonated Indulines.*	*e.g.,* Water-soluble Nigrosines.

* The Indulines and Safranines differ in their basicity ; the former can be liberated by ammonia and extracted by ether, whilst potash is necessary to obtain Safranine base.

TABLE D.

Group III.—Dyestuffs not reduced by Stannous Chloride and Hydrochloric Acid having the Imido quinone carbon chromophore N : R : C :

Branch 1	Branch 2	Description	Class	Formula	Example
The aqueous or alcoholic solution of the dyestuff is treated with potash lye, and then extracted with ether. — Coloured or colourless solution. The colour is extracted by 5 per cent. acetic acid. *Basic dyestuffs.* Dye wool from an alkaline (NH₃) bath.	The aqueous dyestuff solution is boiled with bleached cotton. — The cotton is not dyed.	Colourless, non-fluorescent, ethereal solution. The solution in acetic acid is non-fluorescent. The aqueous solution is decolorised by potash and decomposed by hydrochloric acid,	*Auramines,*	$C\!\genfrac{}{}{0}{}{R}{R}\!=N-$	e.g., Auramine O.
		Colourless, greenish, fluorescent, ethereal solution. The aqueous solution is precipitated by potash, and only slightly changed by hydrochloric acid. Nitric acid colours it red,	*Acridines,*	$-C\!\genfrac{}{}{0}{}{R}{R}\!\diamond N$	e.g., Phosphine.
The colour is not extracted by acetic acid from the coloured ethereal solution. *Neutral dyestuffs.* Insoluble in water; soluble in water.		Colourless or coloured non-fluorescent ethereal solution. The acetic acid extract is reddish-violet, blue, and green, without fluorescence. The aqueous solution is generally decolorised by potash on warming, and is turned yellow by hydrochloric acid (with the exception of the phenylated rosanilines),	*Rosanilines* (unsulphonated),	$C\!\genfrac{}{}{0}{}{R}{R=N}$	e.g., Magenta.
		The ethereal solution is colourless, and does not fluoresce. The solution in acetic acid is pink and fluorescent. The aqueous solution is decolorised by potash.	*Pyronines* (are turned yellow by hydrochloric acid). *Rhodamines* (unsulphonated, are unaffected by hydrochloric acid).	$-C\!\genfrac{}{}{0}{}{R}{R}\!O$	e.g., { Pyronine G. / Rhodamine S. }
		The ethereal solution is yellow, and does not fluoresce. The alcoholic solution is yellow and non-fluorescent, and is unaltered by aqueous acids or alkalies.	*Quinophthalones** (unsulphonated),	$-C\!\genfrac{}{}{0}{}{R}{R=N\equiv}$	e.g., Spirit-soluble Quinoline Yellow.
The ethereal solution is colourless; acetic acid does not extract anything. *Acid dyestuffs.* All soluble in water, and dye wool from an acid (HCl) bath.	The cotton is dyed.	Yellow dyestuffs soluble in water without fluorescence, unchanged by aqueous acids or alkalies.	*Sulphonated Quinophthalones.*		e.g., Water-soluble Quinoline Yellow.
		Water soluble dyestuffs, reddish-violet, blue, or green, generally decolorised by potash lye, little affected by hydrochloric acid,	*Sulphonated Rosanilines.*		e.g., Magenta S.
		Red or violet dyestuffs giving fluorescent aqueous solutions not affected by potash, or only slightly,	*Sulphonated Rhodamines.*		e.g., Violamine R.
		Yellow or orange dyestuffs giving more or less fluorescent aqueous solutions, dyeing silk, wool, and cotton directly,	*Thiazols†*	$-C=N$ / $S-R$	e.g., Primuline.

* The chromophores of the quinoline dyestuffs, Berberine and Flavaniline, are not as yet understood, they are probably compounds intermediate between the auramines and acridines.

† The thiazol dyestuffs are generally sulphonated, with the exception of Thioflavine T, which, although soluble in ether, dyes wool from an alkaline bath.

TABLE E.

Group IV.—Dyestuffs not Reduced by Stannous Chloride and Hydrochloric Acid having the Oxyquinone carbon chromophore O : R : C :

The alcoholic solution of the dyestuff is treated with a few drops of a dilute (1 : 1000) solution of ferric chloride.

— Remains unchanged. *Non-amidated triphenyl-methane dyestuffs,* generally soluble in water, and usually dyeing wool directly.

The dyestuff is dissolved or suspended in boiling water.

- It does not dye wool directly. Generally insoluble in water, soluble in alcohol without fluorescence, — **Aurines.** — $CO\diagup^{R'}_{R=O}$ — e.g., Aurin.
- Dyes wool directly. Generally soluble in water and alcohol to fluorescent solutions, — *Phthaleïns.* — $C\diagup^{R'}_{R=O}O$ — e.g., Eosin.

— Turns green or olive-green *Oxyketone dyestuffs,* generally insoluble in water, dry fibres indirectly.

The original dyestuff is treated with 1 per cent. potash lye.

- Dissolves with a yellow or reddish-yellow colour. *Monoketones.*

  The alkaline solution is treated with an excess of hydrochloric acid.
  - Usually decolorised (with decomposition) especially on warming. — *Benzophenones.* — $CO\diagup^{R}_{R}$ — e.g., Alizarin Yellow A.
  - Gives an intense yellow without decomposition. — *Flavones.* — $CO\diagup^{R'}_{C:C'}O$ — e.g., Quercetin.

- Dissolves with a red, reddish-violet, blue, or green colour. *Diketones.* (Quinones).

  The alkaline solution is acidified with acetic acid.
  - The free acid is precipitated. Generally soluble in ether and dyeing the fibre indirectly. — *Anthraquinones* (unsulphonated). — $CO\diagup^{R}_{R'}CO$ — Alizarin.
  - The dyestuff acid remains in solution, is insoluble in ether and dyes wool directly. — *Anthraquinones* (sulphonated). — Alizarin Red S.

may be recognised by boiling the solution with potash and zinc dust, and examining the filtrate after neutralisation with acetic acid, for bromine or iodine. An alternative method is to heat the dyestuff with lime to redness, dissolve in nitric acid, and examine the solution for the halogen. The detection of *sulphur* to distinguish, for example, *thiazines* from *oxazines* is effected by fusing the dyestuff with potassium nitrate, dissolving, and examining the filtrate for sulphates. If the dyestuff be reducible by stannous chloride, the solution is freed from tin by sulphuretted hydrogen, and the filtrate is examined for the reduction product. Thus, *picric acid* yields triamidophenol, which on treatment with ferric chloride gives blue amidodiimidophenol. *Azo dyestuffs* on reduction give at least two primary amines, which frequently can be separated by ether. The reduced solution, after removing the tin, is treated with an excess of potash, and extracted with ether. The unsulphonated amines are removed, whilst the sulphonated amines remain in the aqueous solution. The latter can be recognised by giving characteristic azo compounds with certain diazo derivatives. For example, sulphanilic acid, obtained by reducing naphthol orange, gives, when combined with tetrazodiphenyl chloride, a yellow tetrazo dyestuff; naphthionic acid gives *Congo red*, and certain hydroxy sulphonated amines, such as $2:1':3'$, $C_{10}H_5.NH_2.OH.SO_3H$, give a violet colour (*diamine black R*, &c.). The presence of a *p*-diamine is recognised by the thiazine reaction (ferric chloride and hydrochloric acid in presence of sulphuretted hydrogen), and in non-amidated dyestuffs this reaction affords a means of distinguishing between mono and disazo dyestuffs. It is also possible to decide in this case whether a sulphonic acid group is in the side or middle ring, since in the former case a thiazine is formed which, in presence of potash, can be extracted by ether, whereas a sulphonated thiazine remains in the aqueous solution.

The two chief reagents suggested by Rota for the analysis of mixtures are ether and wool. With regard to separations by the former, 100 c.c. of the dyestuff solution are treated with 1 c.c. of 20 per cent. potash lye, and then extracted with three times the volume of ether, which is repeated until the ether is colourless, even after acidifying with acetic acid. The aqueous alkaline solution containing the acid dyestuffs is neutralised with acetic acid and subsequently examined. The ethereal solution is washed with very slightly alkaline water, and extracted with one-third of its volume of 5 per cent. acetic acid, which is then evaporated on the water bath; the residue contains the basic dyestuffs. Some dyestuffs, even after extraction with acetic acid, remain in the ether, which in this case is itself evaporated. In presence of caustic potash it frequently happens that some (very few) acid or rather neutral dyestuffs pass into the ether—*e.g.*, spirit soluble *quinoline yellow*, *indophenol blue*, the different *sudans*, &c. In extracting with ether, the choice of an alkali is not immaterial. The *safranines*, for example, require potash, whilst the *magentas* are basified by ammonia; the *indulines*, *oxazines*, and *acridines* are basified by very dilute ammonia, whilst others like *chrysoidine, Bismarck brown, rhodamine S, Victoria blue*, &c., are dissociated in their dilute aqueous solutions. Hence the dilute aqueous solution is first extracted with ether, then treated with 1 per cent. ammonia and extracted subsequently with concentrated ammonia, and finally with 20 per cent. potash lye. A further separation depends upon a difference of solubility in water and ether. When the ethereal solution is shaken with an equal volume of water some dyestuffs are extracted, whilst others less soluble, or quite insoluble, remain in the ether. *Acridine yellow* can in this way be separated from *phosphine*. By means of successive extractions with ether, the acid dyestuffs contained in the original aqueous solution fall into three groups:—(1) Those extracted by ether in presence of 1 per cent. acetic acid, (2) those extracted in presence of sulphuric or hydrochloric acid, and (3) those insoluble in ether. In this way it is possible to separate *erythrosine* from *roccelline* and from *Bordeaux B*, and *direct yellow* from *Congo brown* and *Congo red*. If the mixture consists exclusively of acid dyestuffs, a fourth group has to be taken into consideration—viz., dyestuffs having so feebly an acid character that they can be extracted from the neutral solution by ether, like *sudan I, orchil*, and *sudan G*. In this manner sudan G can be separated from *Victoria yellow*, and *orchil* from *eosin*. Moreover, by extracting the ethereal solution with water, a further separation can be effected; for example, *picric acid* from *Martius yellow* (dinitronaphthol is only very slightly soluble in water), and *diamond black* from *naphthol orange*. The fractional addition of ammonia may also be resorted to. When the separation cannot be effected by ether, recourse is had to wool. All basic dyestuffs are taken up by woollen fibres from a faintly alkaline or neutral bath, whilst acid dyestuffs are left in the bath. The solution of the dyestuff (1:1000) is made alkaline with ammonia (4 to 5 drops per 100 c.c. of solution), and a skein of wool is immersed in it and boiled for three to five minutes. A second skein is then immersed, and, if necessary, a third, so long as the wool is dyed. The solution contains

the acid dyestuffs. The wool is boiled first in very weak ammonia, subsequently in pure water, and is then extracted with hot 5 per cent. acetic acid. This solution is evaporated on the water bath, when the basic dyestuffs remain as a residue. Either the dyeing or extraction can be carried out fractionally, since some dyestuffs attach themselves or are removed more easily than others. Wool acts more effectively in the separation of acid dyestuffs. A 0·1 per cent. solution of the dyestuff is acidified with hydrochloric acid (4 to 5 drops of concentrated hydrochloric acid per 100 c.c.), and successive skeins of wool are immersed for three to five minutes in the boiling solution, as above. The solution contains the mordant dyestuffs. The skeins are washed first with dilute hydrochloric acid, subsequently with water, and are finally extracted at the boil with 5 per cent. ammonia, which then contains the direct dyestuffs. A complete separation is only effected by repeating this treatment, since some of the indirect dyestuffs are absorbed by the fibre.

By dyeing in a neutral or more or less strongly acid bath further separations can be carried out. For example, the following dyestuffs can be separated :—

Dye from neutral bath.	Dye from acid bath.
Alkali violet. Acid violet 4 B N. Orchil.	Ponceau 6 R B. New coccine. Bordeaux B.

With a strongly acid solution (1 c.c. hydrochloric acid per 200 c.c. of solution) the following separations may be made :—

Dye from strongly acid bath.	Dye from weak acid bath.
Bordeaux S. Bordeaux B.	Orange G. Methyl orange.

In all these cases the wool is washed with pure water, faintly acid, or strongly acid water, according to the nature of the dyebath, the fibre subsequently being extracted with hot dilute ammonia, which may also be carried out fractionally. In certain cases, when neither ether nor wool give decisive results, it is necessary to employ cotton. Amongst direct basic colours for cotton are *pyronine*, *rhodamine* (partially), and *thioflavine*, whilst acid colours are *curcumine*, the *tetrazo dyestuffs*, &c. For the separation of direct from indirect cotton dyestuffs, the cotton is boiled for ten minutes in the neutral or faintly alkaline (soap) bath, and then repeatedly washed with boiling water. The following dyestuffs can be separated in this manner :—

Dye cotton directly.	Dye cotton indirectly.
Carbazol yellow. Cotton yellow R.	Diamond yellow R. Phloxine B.

By varying the conditions of acidity or the strength of the bath it is also possible to effect separations — *e.g.*, *brilliant congo* is easily dyed from an acid bath with hydrochloric acid, whilst *brilliant yellow* only does so with difficulty. If neither ether, wool, nor cotton lead to separations, other solvents must be made use of, such as petroleum ether, amyl alcohol, chloroform, and the method employed is as given in the case of ether. Thus, by means of petroleum ether, it is possible to separate *eosin* from *Martius yellow*.

H. Huntington [*] has published a series of tables for the recognition of dyes, in which the reactions made use of are—

1. Reaction with concentrated sulphuric acid.

2. Change on diluting this solution.

3. Addition of HCl to aqueous solution of the dye.

4. Addition of NaOH to aqueous solution of the dye.

These tests have been previously used by Schultz and Julius [†] and Green, [‡] but are here arranged in a form very convenient for use.

DETECTION AND IDENTIFICATION OF COLOURING MATTERS ON DYED FABRICS.

The recognition of the colouring matters which have been employed in dyeing a given fabric is frequently a matter of considerable difficulty. If one dyestuff only has been used it may sometimes be identified with little trouble. For instance, the presence of Prussian blue or logwood black is demonstrated with considerable facility and certainty; but, on the other hand, it is sometimes impossible to determine which of several similar dyes have been employed, even when one only has been used—*e.g.*, many of the azo scarlets are so similarly constituted that it is practically impossible to identify them. An examination of their reduction products would sometimes afford a method of identification, but such work is quite impracticable with the small amounts of dyed material usually available.

When two or more colouring matters are (as is usually the case) present, the difficulty

[*] *Year Book for Colourists and Dyers*, vol. i., 1898.

[†] *Tabellarische Übersicht der Künstlichen Organischen Farbstoffe*.

[‡] English edition and extension of the above.

of identification is greatly increased, since the characteristic reactions of one dyestuff may be masked by the presence of a second. In the examination of a mixture of inorganic bodies the same difficulties would, of course, be met with. For instance, in a solution containing ferric and calcium chlorides, the white precipitate of chalk obtained by adding sodium carbonate to the solution would, in small amounts, be entirely obscured by the brown precipitate of ferric hydrate. In the case of inorganic substances, such difficulties are eliminated by adopting a systematic method of analysis, based upon the classification of the metals and acids into groups having certain reactions in common, the individual members of each group being afterwards identified by special reactions. On the other hand, when dealing with the simplest organic bodies, such as the common organic acids, difficulties in identification are at once encountered; the selection and use of "group-reagents" being impossible, because the presence of one substance may not only mask, but may alter, or actually reverse the normal reactions of a second body. It is therefore no matter of surprise that the identification of such complex organic compounds as colouring matters should present great difficulties. The general plan adopted in the detection of dyes is, if possible, to determine in the first place the group or groups of colouring matters to which those present belong, and this is greatly facilitated by the investigator's knowledge and experience, which frequently enable him at once to fix upon the probable group. For example, no dyeworks chemist would expect a bright red on *cotton* to be dyed with an acid scarlet or with cochineal, but it might be either Turkey-red, a direct cotton colour, a developed azo dye, or a basic dye. On the other hand, a bright red on *wool* might be an acid, a direct, a basic, an alizarin, or cochineal dye, but would probably not be a developed azo compound. The first step should usually be to determine whether a metallic mordant has been employed, since this greatly narrows the field of inquiry. For example, if a bright red on *wool* was found to contain *chromium* as mordant, this would at once point to the presence of an azo mordant dye (cloth red, &c.). If *aluminium* was found, alizarin would be the most likely dye, while *tin* would probably indicate cochineal.

Examination of Dyed Material for Metallic Mordants.—One or two square inches of the material, or a few yards of yarn, are incinerated in a platinum or porcelain crucible until no carbonaceous matter remains. The ash is then tested for metals as follows :—

Iron.—The ash will have a reddish-brown colour. Dissolve in a little nitric acid, dilute with water.

Ammonia, brown precipitate.
Potassium ferrocyanide, blue precipitate.
Ammonium sulphocyanide, red coloration.
Tannic acid, grey or black coloration.

Chromium.—Ash brownish-green. Add to the dry ash a small quantity of powdered potassium nitrate and potassium hydrate; fuse. A bright yellow mass is obtained. Dissolve this in water and add a few drops of acetate of lead solution, when a yellow precipitate of chromate of lead will be formed.

Aluminium.—The ash is white or grey. When heated on charcoal with a drop of cobalt nitrate a blue mass is obtained. Dissolve the ash in hydrochloric acid, dilute with water and add ammonia, when a white gelatinous precipitate indicates aluminium.

Tin.—Ash white or grey. When fused with sodium nitrate and hydrate it gives a white mass, in the aqueous solution of which hydrochloric acid gives a white precipitate, soluble in excess. From this solution sulphuretted hydrogen throws down a dirty yellow precipitate of stannic sulphide.

Zinc.—Ash white or grey. Dissolve in hydrochloric acid. Ammonium sulphide gives a white precipitate soluble in hydrochloric acid. The ash, when heated with sodium carbonate and then moistened with cobalt nitrate and re-heated on charcoal, gives a bright green mass.

Copper.—Ash usually contains also iron or chromium. Dissolve in nitric acid, add slight excess of ammonia, and filter. The solution is blue. Add acetic acid, then potassium ferrocyanide, when a reddish-brown coloration is produced. Moisten the ash with hydrochloric acid and heat on platinum wire; the flame is coloured green.

It must, of course, be understood that the amount of metal present is very minute, and the reactions obtained are correspondingly faint.

Too much reliance must not, however, be placed on the result of the examination for mordants, because certain mordant dyes—*e.g., nitro-alizarin*—are occasionally employed without mordant; and, on the other hand, metallic oxides may be met with both on white material and on cloth or yarn dyed with non-mordant dyes; metals being employed, for example, in rendering wool unshrinkable and in waterproofing processes. In most cases, however, the presence of a metal in the ash obtained on burning the material affords a strong presumption that the colouring matters used belong to the group of mordant dyes, and further experiment should be first made on this assumption.

If the dyestuff under examination is not a mordant dye, an endeavour should be made to determine to what group of colouring matter it does belong, and this may usually

be done by the use of acid or alkaline reducing agents, which give the following results :—

(a) *The colour is destroyed, but quickly reappears on exposure to air*—Azines, oxazines, thiazines, acridines.

(b) *Decolorised, but the colour is restored by oxidising agents*— Rosaniline dyes and phthaleïnes (eosins).

(c) *Permanently decolorised* — Azo dyes, nitro compounds, and nitroso derivatives.

(d) *The dye is unaffected*—Alizarin dyes, primuline, and a few others.

The mode of applying the reducing solution is as follows :—Boil a small piece of the dyed material in water in a test tube, and if nothing is removed, add a few drops of ammonia and again boil. Remove the cloth and neutralise the ammoniacal solution with acetic acid. If either water or ammonia remove any colour, add to the solution a few drops of hydrochloric acid and note any change which may occur, then add a few drops of a 10 per cent. solution of stannous chloride. If necessary, the solution is heated to the boil, and if it is not then decolorised the dye or dyes present belong to group (d) above. If decolorised, the solution is neutralised (not rendered alkaline) with ammonia, and, after allowing the precipitate to subside, is exposed to the air for a few minutes, when if the original colour is restored, a colouring matter belonging to class (a) is present. If mere exposure to air does not restore the colour, a drop of chromic acid or ferric chloride solution is added, by which means the colour of dyes belonging to class (b) will be restored. If neither of these re-develop the colour, it is " permanently decolorised." (class c.)

In this manner groups a, b, c, d are distinguished in those cases in which it is possible to remove a portion of the colouring matter from the dyed material. Where this is not possible, it is necessary to apply the reducing agent to the material itself, and this is best done as follows :—Boil a small portion of the material in water, pour off the water, add a little cold water, then a little hydrochloric acid and stannous chloride solution as before. Heat if necessary, pour off the solution, and proceed as above described ; but if the material is decolorised, it is well to try the re-oxidation tests both on it and on the solution.

Having thus determined to what group the dye used in any particular case belongs, the field of enquiry is much narrowed, and before making further tests it is desirable to obtain small pieces of material—wool, silk, or cotton, as the case may be—dyed with these colouring matters which experience suggests as being the most likely to be present on the sample under examination. Parallel tests are then to be made upon the sample and upon the material dyed with

known colouring matters, various reagents being applied upon small portions of the material.

The reagents employed are various, and tables giving the reactions of the more important dyestuffs will be found in Knecht, Rawson, and Loewenthal's *Manual of Dyeing*, in Hummel's *Dyeing of Textile Fabrics*, in Thorpe's *Dictionary of Applied Chemistry* (vol. i., p. 586), and in other books on dyeing. The reactions of many dyes recently introduced will be found in Lehne's *Farber Zeitung*, 1890-91, pp. 186, 226, 260, 318, 388 ; 1891-92, pp. 168, 276, 358 ; 1892-93, pp. 50, 198, 248, 332 ; 1893-94, pp. 216, 254, 350 ; 1894-' 5, p. 22. A series of tables for detecting dyes on silk is given by B. Martinon (*Journ. Soc. Dyers and Colourists*, 1887, p. 124).

These tables are very useful for reference, but cannot be relied upon to give conclusive results, which can indeed only be obtained by proceeding in the manner above described and making simultaneous and parallel tests with material dyed with known colouring matters.

The following series of reagents has been found by Gardner to be convenient and sufficiently extensive. The tests should be used in the order given, and are best applied as follows :—

Application of Cold Reagents.—Steep a piece of material (say) $\frac{1}{2}$ inch square in (say) 5 c.c. of reagent for five minutes in a small porcelain dish.

Application of Reagents by Boiling.—In a test tube put 10 c.c. of reagent and a piece of material 1 inch by $\frac{1}{2}$ inch. Boil *gently* for five minutes.

Application of Nitric Acid.—Place a piece of material 1 inch by $\frac{1}{2}$ inch on a white glazed porcelain plate, and spot by dipping a small glass rod into the acid and then pressing it on to the cloth. Observe and note the changes which occur during the formation of the spot, and re-examine after several hours, noting any further change.

List of Reagents.

1. Boiling water.

1a. If any colour is removed, repeat 1 with fresh water on the same piece of material.

2. Boiling alcohol.

3. Nitric acid, 63° Tw. (spot).

4. Hydrochloric acid, 32° Tw. (cold).

5. Sulphuric acid, 168° Tw. (cold).

6. Sulphuric acid, 168° Tw., 5 c.c. per litre (boiling).

6a. Repeat 6 if any colour is removed.

7. Sulphuric acid, 168° Tw., 50 c.c. per litre (boiling).

7a. Repeat 7 if any colour is removed.

8. Sodium hydrate, 35° Tw. (cold).

9. Ammonia, 0·88 sp. gr. (cold).

10. Borax, 10 grms. per litre (boiling).

11. Chromic acid solution (boiling)—

10 grms. K$_2$Cr$_2$O$_7$ per litre.
3·5   „   H$_2$SO$_4$, 168° Tw. per litre.
      (Acid oxidising agent).

12.   1 grm. sodium peroxide per litre.
2·4 grms. magnesium sulphate per litre.
      (Alkaline oxidising agent).

Apply at 50° C. If no action, boil.

13. Bleaching powder solution, 8° Tw. (cold).

14. Sulphurous acid (boiling)—

5 c c. NaHSO$_4$, 60° Tw., 10 grms. per litre.
5 „   H$_2$SO$_4$, 168° Tw., 3·5 „   „
      (Acid reducing agent).

15. Stannous chloride solution—

20 grms. SnCl$_2$. 2H$_2$O per litre.
100 c.c. HCl, 32° Tw.   „
      (Acid reducing agent).

Apply cold. If no action, boil.

16. Ammonium sulphide solution—

100 grms. per litre.
      (Alkaline reducing agent).

17. Nitrous acid (boiling)—

5 c.c. NaNO$_2$, 5 grms. per litre.
5 „   H$_2$SO$_4$, 168° Tw., 3·5 grms. per litre.

18. Apply test 17 cold, then wash and steep the material in a solution of beta-naphthol, 5 grms. per litre.

COBALT, Co . = 59. Cobalt occurs in nature associated with sulphur and arsenic. The metal is obtained by treating the tetroxide Co$_3$O$_4$ with charcoal. Its specific gravity is 8·9 ; it is not easily melted. It has a reddish-white colour and is magnetic. The metal resembles nickel in many respects. The compounds of cobalt are notable for their bright colour, which, moreover, they are capable of imparting to pigments. Glass of a brilliant blue tint is prepared by addition of cobaltic salts. Cobaltous salts (derived from CoO) have a pink colour.

Cobalt Sulphate, CoSO$_4$ + 7H$_2$O, forms red crystals, and is occasionally used as a mordant for wool.

COCCERIN v. COCHINEAL (CARMINE RED).

COCCININ (M.). *Phenetol red.* An obsolete azo acid dyestuff.

COCCININ B (M.). An azo compound.

Amido para cresol __ Beta naphthol
methyl ether   disulphonic acid R.

1878. Dark red powder, giving cherry-red solution in water. In concentrated H$_2$SO$_4$, cherry-red solution, unchanged on dilution.

Application.—An acid colour. Dyes *wool* or *silk* red from an acid bath.

COCHINEAL. This dyestuff is indigenous to Mexico, where it was found to be in use by the natives when the Spaniards first entered the country in 1518. Recognising its importance, they commenced its cultivation ; and it was exported to Europe about 1550, where it rapidly superseded kermes.

Origin.—The insect known as cochineal is the *Coccus cacti* (*Hemiptera*). It feeds on various species of *Cactaceæ*, more particularly on the Mexican "nopal" plant (*Cactus opuntia* or *C. coccinilifera*). The male and female insects are very dissimilar in appearance, the former being slender in form, red in colour, having a small head, two horizontal wings, six legs, and two long diverging hairs projecting from the abdomen. On the other hand the female insect, which is much the most numerous, is similar in appearance and size to the "lady bird." Its body is hemispherical, and of a dark reddish-brown colour ; it has six rudimentary legs but no wings, and is practically incapable of locomotion.

The cultivation of cochineal is carried on in Mexico, Peru, Algiers, The Canaries, and the south of Spain, the cultivated insect distinguished as *Grana fina* being about twice the size of the *Grana sylvestra*, which is obtained from the wild cactus.

The female insects are removed from the plants shortly before the time of egg-laying and killed, and the method of killing gives rise to two other commercial varieties. If the insects are stoved, their natural white powdery covering is retained, and "silver-grey" cochineal is the result ; but if killed by means of steam or hot water, they lose this appearance and "black" cochineal is produced.

The dyestuff requires absolutely no preparation for the market, but before being used by the dyer the insects are beaten or ground to powder.

The structure of the cochineal insect may be made visible by immersing a few of the dried insects in warm water for several hours.

Colouring Matters.—Cochineal is relatively rich in colouring matter compared with most of the other natural dyes, containing from 10 to 20 per cent. of the pure substance. The latter exists in the dried insect—principally in the eggs—as a glucoside *carminic acid*, from which the true colouring matter, *carmine red*, is readily produced.

Carminic acid, C$_{17}$H$_{18}$O$_{10}$, is a purplish-red amorphous substance, which forms crystalline salts (*carminates*) with the alkalies or alkaline earths. It is soluble in water, alcohol, or benzene, but insoluble in ether, and may be prepared as follows :—Ground cochineal is treated with ether to remove fat, and is then extracted with *boiled* water. The colouring principle which is thus extracted is precipitated by acetate of lead, and the lead salt, after washing, is decomposed by sulphuretted hydrogen. The solution of impure carminic acid thus obtained is filtered and evaporated to dryness, and the substance is purified by dissolving in alcohol and precipitating by ether.

It is interesting to note that carminic acid is not only found in several insects, but also in some plants—*e.g.*, *Monada didyma*.

Carmine red, $C_{11}H_{12}O_7$, is obtained by boiling a dilute aqueous solution of carminic acid with a few drops of mineral acid; an optically inactive, non-fermentable, non-crystalline sugar being produced at the same time. Carmine red is a dark purplish amorphous substance, which forms colour lakes of very varied hues with different metals—*i.e.*, with *tin* a scarlet, with *aluminium* a crimson, and with *iron* a grey pigment. When carmine red is treated with nitric acid, *nitro-coccussic acid* ($C_8H_5(NO_2)_3O_3$) and *oxalic acid* are produced. The first-mentioned substance is easily obtained synthetically, being *trinitrocresotic acid* ($C_6(CH_3).(OH).(NO_2)_3.COOH$), but carmine red itself has not yet been artificially produced. A saponifiable fat, *coccerin*, also exists in cochineal, the amount varying from 0·5 to 4 per cent.

Ammoniacal Cochineal.—This substance is a definite compound, produced by the action of ammonia on carminic acid, according to the following equation:—

$$C_{17}H_{18}O_{10} + 2NH_3 =$$
$$C_{17}H_{20}O_5N_2 + 2H_2O.$$
Carminamide.
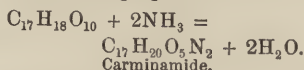
It is readily obtained by mixing together 1 part of finely-ground cochineal and 5 to 6 parts of strong ammonia, and allowing the mixture to stand in a warm place for two or three weeks. It is then evaporated to dryness and ground to powder.

Uses.—In addition to its use in dyeing, cochineal is largely employed in the manufacture of artists' pigments, the cochineal lakes being very stable under the action of the light, &c. The chief of these bodies is *cochineal carmine*, which may be prepared by extracting 1 lb. of ground cochineal with 2 gallons of water, in which 1 oz. of cream of tartar has been dissolved; the filtered liquid is allowed to stand for several days, during which time it deposits about an ounce of bright carmine.

The *aluminium* and *tin* lakes are also used as pigments.

Cochineal is almost exclusively used for the production of scarlet shades on wool in conjunction with tin mordant. It also yields crimson shades with alum mordant. The colours are faster to light than those obtained from most of the natural dyewares.

Valuation.—The relative value of samples of cochineal may be determined by a comparative dye trial, or by titrating a filtered solution of the colouring matter, in distilled water, with a standard solution of somewhat basic alum.

COCHINEAL RED A (B.). *Crocein scarlet 4 B or G* (K.), *Brilliant scarlet* (Lev.), *Brilliant ponceau 4 R* (C.) (By.), *New coccin A* (Ber.) (M.), *Scarlet* (F.). An azo compound.

Naphthionic acid —   *Beta-naphthol gamadisulphonic acid.*

1878. Scarlet powder, easily soluble in water. In concentrated H_2SO_4, magenta-red solution, becoming yellowish-red on dilution.

Application.—An acid colour. Dyes *wool* and *silk* cochineal-red from an acid bath.

COCHINEAL SCARLET G (Sch.). An azo compound.

Aniline —   *Alpha-naphthol sulphonic acid C.*

1883. Brick-red powder, giving yellowish-red solution in water. In concentrated H_2SO_4, cherry-red solution; on dilution, brownish-red ppt.

Application.—An acid colour. Dyes *wool* brick-red from an acid bath.

COCHINEAL SCARLET P S (By.) *v.* PALATINE SCARLET.

COCHINEAL SCARLET 2 R (Sch.). An azo compound.

Toluidine —   *Alpha-naphthol sulphonic acid C.*

1883. Cinnabar red powder, slightly soluble in cold, easily in hot, water, giving yellowish-red solution. In concentrated H_2SO_4, magenta-red solution; on dilution, red ppt.

Application.—An acid colour. Dyes *wool* red from an acid bath.

COCHINEAL SCARLET 4 R (Sch.). An azo compound.

Xylidine —   *Alpha-naphthol sulphonic acid L.*

1883. Bright red powder, slightly soluble in water. In concentrated H_2SO_4, magenta-red solution; red ppt. on dilution.

Application.—An acid colour. Dyes *wool* red from an acid bath.

COERULEÏN (B.) (D. & H.) (By.). *Coeruleïn A* (M.), *Alizarin green*, *Anthracene green*. Produced by *action of sulphuric acid on gallein* at 200° C. 1871. Black paste, insoluble in water or alcohol. In concentrated H_2SO_4, dull yellowish-brown solution; on dilution, reddish-brown, then green with black ppt.

Application. — A mordant dye. Dyes chrome-mordanted *wool* or *cotton* dark green. Colour extremely fast to all agencies.

COERULEÏN S or S W in PASTE or POWDER (B.) (By.) (M.) (D. & H.) (F.). Sodium bisulphite (2 mols.), compound of coeruleïn (1 mol.). 1879. Brown paste or black powder, slightly soluble in cold, more easily in warm, water, giving a dirty greenish-brown solution. Slightly soluble in hot alcohol. In concentrated H_2SO_4, dark brown solution; black ppt. on dilution. The compound is decomposed at about 75° C., insoluble coeruleïn being regenerated.

Application.—A mordant dye. During the dyeing process the above decomposition occurs, the dyed colour being identical with that produced by insoluble coeruleïn. The better solubility of the bisulphite compound renders it more suitable for *wool* dyeing.

COFFEE BEANS, when unroasted, contain a substance (viridic acid) which dissolves in sulphuric acid with a crimson colour, and gives a bright green solution in alkalies. This substance dyes wool and silk green.

COLLODION *v.* COTTON (ACTION OF ACIDS).

COLLODION SILK *v.* ARTIFICIAL SILK.

COLORIMETRY. The relative value of solutions of many dyes and dyewares may often be determined with approximate accuracy by observing the depth of colour of equal layers of the solutions in ordinary Nessler tubes of 100 c.c. capacity.

If pure coal-tar colours are to be examined, 50 milligrams of colouring matter per litre will be sufficient. If equal weights of two samples be dissolved in equal volumes of water, 10 c.c. of the standard colour are placed in one cylinder and diluted to 100 c.c. with distilled water, then, say, 10 c.c. of the solution to be compared with this are run from a burette into a test glass and similarly diluted. The two cylinders are placed on white tiles and the depth of colour observed by looking downwards through the solutions. A number of experiments must be made, using more or less than 10 c.c. until the same depth of colour is reached in both cases. The relative value of the two samples is in the inverse proportion to the number of c.c. required. In some cases colours which give a similar shade and depth of tint when examined as above produce different results in dyeing. The impurities in many dyewares also obscure the true colour of the dyeing principle.

Another arrangement is also in use having the same object in view—viz., Nessler tubes provided with a side tube and stopcock near the base. The cylinders, which must be accurately graduated, are filled to the 100 c.c. mark with the solutions to be compared, and, after observation, a little of the solution which exhibits the darker shade is run off. This operation is repeated until the solutions show exactly the same depth of colour. The volume of the liquids is then observed and the figures will denote the inverse ratio of the value of the two samples. If 100 c.c. of one sample show the same tint as 80 c.c. of the other, the relative value of the two solutions will be as 80 : 100. In this method the diameter of the tubes must be the same throughout their entire length.

The Tintometer is an instrument invented by J. W. Lovibond * for the matching, analysis, synthesis, and measurement of colour.

* *Journ. Soc. Dyers and Col.*, 1887, p. 186.

It gives two fields of view under exactly similar monocular conditions, freed from all errors arising from unequal side lights and the different power of distinguishing which may exist in the eyes of the observer. A series of standard coloured glass slips is used, each set being of the same colour but varying regularly in depth of tint. Each slip is numbered, and by superimposing several slips it is possible to match any shade, and, the numbers having been carefully recorded, reproduce that particular tint at any future time. The value of the instrument as a colour recorder will be obvious to the colour and extract manufacturer. In testing colouring matters, alcohol, water, or other solvent may be used, and the resulting solution placed in the glass cell provided with the instrument. These cells vary from $\frac{1}{8}$ inch for dark liquids up to 2 feet for pale solutions. When the cell is in position standard glasses are placed in the instrument until the tint is correctly matched.

The instrument can also be used for measuring the colour of opaque objects.

COLUMBIA BLUE R (Ber.). Dark bluish powder. Aqueous solution reddish-blue. Alcoholic solution violet. Concentrated H_2SO_4, bright blue solution; on dilution, red-violet solution.

Application.—Direct cotton dye, suitable for *union* material.

COLUMBIA BLUE G (Ber.). Similar to above.

COLUMBIA FAST BLUE 2 G (Ber.). Similar to above.

COLUMBIA CHROME BLACK 2 B (Ber.). Black powder. Aqueous solution red-blue. Alcoholic solution blue. Concentrated H_2SO_4, dull blue; on dilution, violet-blue.

Application.—A direct cotton colour fixed by subsequent chroming.

COLUMBIA BLACK B (Ber.). Black powder. Aqueous solution reddish-blue. Insoluble in alcohol. Concentrated H_2SO_4, dull blue; on dilution, bluish-violet solution.

Application.—A direct cotton dye, suitable for *cotton* or *union* material.

COLUMBIA BLACK FF, FB, FBD, R, 2BW, 2BX (Ber.) are similar to the above.

COLUMBIA BROWN R (Ber.). Brownish-black powder. Aqueous solution dull bluish-red. Alcoholic solution brownish-red. Concentrated H_2SO_4, bright blue; on dilution, violet, bluish-red, then brownish-red.

Application.—A direct cotton dye. Dark brown shades, which become darker on diazotising and developing with phenylene diamine.

COLUMBIA GREEN (Ber.). Greyish-black powder. Aqueous and alcoholic solution bluish-green. Concentrated H_2SO_4, violet solution; on dilution becomes dull blue, then bluish-green.

Application.—A direct cotton dye, producing bluish-green shades on unmordanted *cotton.*

COLUMBIA ORANGE R (Ber.). Reddish-brown powder. Aqueous solution brownish-yellow. Alcoholic solution yellow. Concentrated H_2SO_4, violet solution; on dilution becomes brown, then yellow.

Application.—A direct cotton dye, producing brownish-orange shades on unmordanted *cotton.*

COLUMBIA RED S B (Ber.). Reddish-brown powder. Aqueous solution bluish-red. Alcoholic solution yellowish-red. Concentrated H_2SO_4, bluish-red solution; unchanged on dilution.

Application.—A direct cotton dye, producing bright bluish-red shades on unmordanted *cotton, wool,* or *union* material.

COLUMBIA YELLOW (Ber.). Brownish-yellow powder. Aqueous or alcoholic solution bright yellow. Concentrated H_2SO_4, dark red solution; on dilution gradually changes to yellow.

Application.—A direct cotton dye. Gives brownish-yellow shades on unmordanted *cotton.*

CONDITIONING. Silk and wool have the property of absorbing moisture to a large amount, and the percentage present is continually varying according to the hygrometric condition of the atmosphere. Therefore since these fibres are sold by weight it is necessary for the buyer to know their " condition " as regards moisture at the time of purchase. The recognition of this necessity has led to the establishment of official " conditioning houses" in many centres of the silk trade—*e.g.,* Lyons, S. Etienne, Paris, Crefeld, Zurich, London, &c., and (more particularly for the valuation of wool) in Bradford.

Silk.—In the conditioning of *silk* the whole bulk is weighed, and then sample hanks are taken from various parts weighing altogether about 1500 grms. This sample is divided into three lots, two of which are accurately weighed and then dried in a specially constructed apparatus by means of a current of air heated to 110° to 112° C. until the weight is constant. If the results are within $\frac{1}{2}$ per cent. of each other the mean is taken, if not the third lot is similarly dried. The "condition" of the silk is then arrived at by adding to the absolute dry weight, which is calculated from the loss of weight, the legal amount of moisture—viz., 11 per cent.

Wool.—The conditioning of *wool* frequently involves other determinations besides that of moisture.

Moisture is estimated in a similar manner to that above described, but the temperature should not be allowed to exceed 105° C.

Yolk in raw wool is determined by extracting first with alcohol and ether, then with water, and drying.

Oil added in spinning is estimated by extracting with ether in a Soxhlet apparatus. (Of course, yolk and oil will not both be present.)

A great variety of other work is also carried out in conditioning houses, such as the investigation of the cause of defective yarn and cloth, &c., &c.

CONGO COLOURS *v.* DIRECT COTTON DYES.

CONGO, CONGO RED (Ber.) (By.) (L.) (Lev.). An azo compound.

$$Benzidine\!\!<\!\!\begin{array}{l}Naphthionic\ acid.\\ Naphthionic\ acid.\end{array}$$

1884. Reddish-brown powder, soluble in water. In concentrated H_2SO_4, blue solution; blue ppt. on dilution.

Application.—A direct cotton colour. Dyes *cotton* (and *wool*) red from an alkaline salt bath. Extremely sensitive to acids, which turn it blue.

CONGO G R (Ber.) (By.). An azo compound.

$$Benzidine\!\!<\!\!\begin{array}{l}Naphthionic\ acid.\\ Meta\text{-}amidobenzol\ sulphonic\\ \quad acid.\end{array}$$

1885. Brown powder, giving brownish-red solution in water. In concentrated H_2SO_4, blue solution; on dilution, blue ppt.

Application.—*v.* CONGO RED.

CONGO P (Ber.) (By.). An azo compound.

$$Benzidine\!\!<\!\!\begin{array}{l}Phenol.\\ Beta\text{-}naphthol\ disulphonic\\ \quad acid\ G.\end{array}$$

1886. Red powder, soluble in water. In concentrated H_2SO_4, violet solution; dark brown ppt. on dilution.

Application.—*v.* CONGO RED.

CONGO 4 R (Ber.) (By.) (L.). An azo compound.

$$Tolidin\!\!<\!\!\begin{array}{l}Naphthionic\ acid.\\ Resorcin.\end{array}$$

1886. Brown powder, giving brownish-red solution in water. In concentrated H_2SO_4, blue; violet ppt. on dilution.

Application.—*v.* CONGO RED.

CONGO BLUE B X (Ber.) *v.* DIAMINE BLUE B X (C.).

CONGO BLUE 2 B (Ber.) (By.). An azo compound.

$$Dianisidine\!\!<\!\!\begin{array}{l}Beta\text{-}naphthol\ disulphonic\\ \quad acid\ R.\\ Alpha\text{-}naphthol\ sulphonic\\ \quad acid\ N\ W.\end{array}$$

1894. A direct cotton blue dye.

CONGO BLUE 2 B X (Ber.) *v.* DIAMINE BLUE 2 B (C.).

CONGO BLUE 3 B (Ber.) *v.* DIAMINE BLUE 3 B (C.).

8

CONGO BROWN G (Ber.) (Lev.). An azo compound.

                Cloth orange — Sulphanilic acid.

1888. Brown powder soluble in water. In concentrated H_2SO_4, reddish-violet solution; on dilution, dark brown ppt.

   Application.—A direct cotton colour. Dyes *cotton* yellowish-brown from a soap bath.

CONGO BROWN R (Ber.) (Lev.). An azo compound.

                Cloth orange — Naphthionic acid.

1888. Appearance, reactions, and application similar to Congo brown G.

CONGO CORINTH B (By.) (Ber.) (L.) (Lev.). An azo compound.

      Tolidin $<$ *Naphthionic acid.*
             Alpha-naphthol sulphonic acid
             N W.

1886. Greenish - black powder, giving magenta-red solution in water. In concentrated H_2SO_4, blue solution; on dilution, violet ppt.

   Application.—A direct cotton colour. Dyes *cotton* brownish-violet from a soap bath.

CONGO CORINTH G (By.) (Ber.) (L.) (Lev.). An azo compound.

      Benzidine $<$ *Naphthionic acid.*
             Alpha-naphthol sulphonic acid
             N W.

1886. Appearance, reactions, and application similar to above.

CONGO FAST BLUE B (Ber.). An azo compound.

              Alpha-naphthol
      Dianisidine $<$ *disulphonic acid.*
      Alpha-naphthol $>$ *Alpha-naphthylamine.*
       disulphonic acid

1890. A direct cotton blue.

CONGO FAST BLUE R (Ber.). An azo dye.

              Alpha-naphthol
      Tolidin $<$ *disulphonic acid.*
      Alpha-naphthol $>$ *Alpha-naphthylamine.*
       disulphonic acid

1890. A direct cotton blue.

CONGO ORANGE G (Ber.). Red powder. Aqueous solution, orange. Alcoholic solution, yellow. Concentrated H_2SO_4, bright blue; on dilution, violet, then brown.

   Application.—A direct cotton dye, producing reddish-orange shades.

CONGO ORANGE R (Ber.) (By.) (L.) (Lev.) An azo compound.

            Beta-naphthylamine disulphonic
      Tolidin $<$ *acid R.*
            Phenetol.

1889. Yellowish - red powder, soluble in water. In concentrated H_2SO_4, dark blue solution; on dilution, dark brown ppt.

   Application.—A direct cotton dye. Dyes unmordanted *cotton* bright orange from an alkaline bath.

CONGO PURE BLUE (Ber.) *v.* DIAMINE PURE BLUE (C.).

CONGO RED *v.* CONGO.

CONGO VIOLET (Ber.) *v.* BORDEAUX EXTRA (By.).

CONGO YELLOW PASTE (By.) (Ber.). An azo compound.

             Sulphanilic acid.
      Benzidine $<$
             Phenol.

1885. Brownish-yellow paste, slightly soluble in water. In concentrated H_2SO_4, brownish-red solution; on dilution, brown ppt.

   Application.—A direct cotton colour, dyeing unmordanted *cotton* dull yellow from a soap bath.

COOMASSIE BLACK B, J (Lev.). *Acid blacks.*

COOMASSIE NAVY BLUE (Lev.). *Acid blues.*

COPPER, $Cu = 63.2$. Copper occurs in the metallic state in considerable quantities, often in the form of cubes and octahedra. The ores of copper are also abundant, *copper pyrites* (Cu_2S,Fe_2S_3), *copper glance* (Cu_2S), and *malachite* (basic copper carbonate) ($2CuCO_3$, $Cu(OH)_2$ being the best known. The metal is obtained from its ores by heating with charcoal, the oxides produced by roasting and otherwise purifying the raw material.

Copper has a characteristic red colour. It is malleable and ductile, and its specific gravity is 8·9. In dry air it is unchanged, but in a moist atmosphere it becomes covered with a layer of basic copper carbonate. On heating strongly, copper becomes covered with a layer of the black oxide, CuO.

When in a finely-powdered state, copper is attacked by hydrochloric acid, hydrogen being evolved. Dilute nitric acid, when cold, attacks copper, forming the nitrate, $Cu(NO_3)_2$, and evolving nitric oxide; the reaction increases in violence with the temperature and the concentration of the acid. Sulphuric acid has no action in the cold, but, when heated, the acid is reduced to sulphur dioxide, copper sulphate being simultaneously produced.

Copper is an exceptionally good conductor of heat and electricity. It is a constituent of many alloys, such as brass, gun-metal, &c.

COPPER ACETATE, $Cu(C_2H_3O_2)_2 + H_2O$. —This salt is prepared by the double decomposition of lead acetate and copper sulphate, or by dissolving hydrated copper oxide or carbonate of copper in acetic acid. It forms dark bluish-green crystals, which effloresce in the air. It is easily soluble in water.

The solution on being boiled evolves acetic acid.

Basic Copper Acetate, $2Cu(C_2H_3O_2)(OH) + 5H_2O$—*Blue Verdigris.*—Basic acetate of copper is formed by exposing sheets of copper to the action of acetic acid or the residues obtained in the manufacture of wine. It forms blue crystals, which are decomposed by water, a more basic salt (*green verdigris*), $2Cu(C_2H_3O_2)_2,CuO$, being produced.

Basic copper acetate occurs in commerce as greenish-blue lumps, containing basic copper carbonate and sometimes calcium sulphate, copper sulphate, and zinc.

Analysis of Copper Acetate.—*Copper* may be determined by igniting a weighed portion of the sample, dissolving the residue in hydrochloric acid, and treating the dilute boiling solution with caustic soda. *Acetic acid* is best estimated by distillation with phosphoric acid (*v.* CALCIUM ACETATE (*Analysis*), p. 71).

COPPER ARSENITE, $Cu(AsO_3)_2$ (*Scheele's green*), is formed by the addition of sodium arsenite to a salt of copper. It has a light green colour.

COPPER CARBONATE, $CuCO_3$, has not been prepared, but a basic salt, $CuCO_3 + Cu(OH)_2$, is obtained when a cupric salt is treated with an alkaline carbonate. The same substance occurs as the mineral *malachite*. Both the natural and artificial products are insoluble in water, and are used as pigments.

COPPER CHLORIDES, $CuCl_2$ and $CuCl$.

Cuprous Chloride, $CuCl$ or Cu_2Cl_2, is prepared by boiling copper turnings and hydrochloric acid with cupric chloride. The salt is precipitated as a white crystalline substance on adding water to the above mixture. It absorbs oxygen on exposure to the air, turning brown. The cuprous salts all oxidise easily and form cupric salts.

Cupric Chloride, $CuCl_2$.—Copper oxide or carbonate dissolves in hydrochloric acid with formation of cupric chloride. This salt is also produced when excess of chlorine is allowed to act on metallic copper. It is easily soluble in alcohol and in water, crystallising from the latter with 2 molecules of water. The crystals have a bluish-green colour and are deliquescent. On heating, the water of crystallisation is driven off, and the anhydrous salt remains as a brownish-yellow powder, which, on further heating, loses an atom of chlorine and leaves a residue of cuprous chloride, $CuCl$.

Cupric chloride is used in the manufacture of *methyl violet*, in *calico printing* and in the oxidation of *cutch colours*.

COPPER NITRATE, $Cu(NO_3)_2$, forms dark blue crystals containing 3 or 6 molecules of water, and is prepared by treating lead nitrate with copper sulphate. Nitric acid also dissolves both metallic copper and copper oxide with formation of the nitrate. On heating the salt it decomposes, oxide of copper and nitrous fumes being produced. It is a strong oxidising agent and is deliquescent and easily soluble in water.

COPPER OXIDES, Cu_2O and CuO.

Cuprous Oxide, Cu_2O (*red oxide of copper*), occurs native as *cuprite*. It may be prepared by heating the black oxide with metallic copper in a finely-divided condition in the absence of air. If an alkaline solution of copper sulphate be boiled with grape sugar or certain other organic substances, cuprous oxide is deposited as a red powder. It is used in the manufacture of glass of a ruby-red colour.

Caustic soda precipitates a yellow hydrated oxide from cuprous chloride, which, in ammoniacal solution, turns blue at once in presence of oxygen, for which it is used as a test.

Cupric Oxide, CuO (*black oxide of copper*).—This is prepared by strongly heating copper turnings with free access of air, or by simply igniting cupric nitrate. It is a black powder, readily soluble in dilute acids. Copper oxide is used as an oxidising agent in organic analysis.

Oxide of copper is, similarly to the hydrate, soluble in ammonia, forming a dark blue solution, which dissolves vegetable fibres (paper, cotton, &c.). The presence of mineral salts in this liquid tends to prevent solution of the cellulose, or to cause its re-precipitation.

Cupric Hydroxide or Hydrate, $Cu(OH)_2$, separates as a voluminous light blue precipitate on the addition of caustic alkalies to cupric salts. On boiling, the hydrate is decomposed, a black precipitate of the oxide CuO being obtained. *Schweizer's reagent,* which possesses the property of dissolving cellulose, is prepared from the hydrated oxide by dissolving it in strong ammonia.

COPPER SULPHATE, $CuSO_4 + 5H_2O$ (*blue vitriol*).

Preparation. — Sulphuric acid dissolves copper with formation of copper sulphate and evolution of sulphur dioxide. On the large scale, copper glance or other ore of copper which contains sulphur is roasted and then dissolved in dilute sulphuric acid. The resulting solution of copper sulphate contains ferrous sulphate in more or less considerable quantity. For many purposes iron is injurious, hence the crude copper sulphate solution is treated with metallic iron, whereby the copper is precipitated.

$$CuSO_4 + Fe = Cu + FeSO_4.$$

The metal is collected, oxidised by heating, dissolved in dilute sulphuric acid, and the salt crystallised. The aqueous solution of copper sulphate is blue.

Properties.—Sulphate of copper forms triclinic crystals of a blue colour. On heating to 100° C., 4 molecules of water are driven off, the last molecule only separating at a temperature of 240° C. The resulting anhydrous copper sulphate is white and is extremely hygroscopic, turning blue in a moist atmosphere, or in liquids containing water. A small quantity of the anhydrous salt thus serves to prove the presence, or otherwise, of water in such substances as alcohol, &c. Copper sulphate forms double sulphates with ammonium and potassium sulphates. 100 parts of water dissolve 40 parts of the salt at the ordinary temperature, and 203 parts at 100°C. Sulphate of copper is used in calico printing and dyeing and in the preparation of many pigments. It is also used in agriculture to prevent the encroaches of various insects. Several insoluble basic sulphates are known. Copper sulphate and other soluble salts of copper in aqueous solution redden blue litmus and have a disagreeable metallic taste. The addition of alkaline carbonates causes precipitation of basic carbonates.

Analysis. — Commercial copper sulphate always contains small quantities of iron.

Estimation of Copper by precipitation as CuO.—0·5 grm. of the sample is dissolved in about 150 c.c. of water in a porcelain basin, and heated to the boiling point. A slight excess of a solution of pure caustic soda is added, and the liquid gently boiled for about five minutes, the basin being covered meanwhile with a clock-glass. The brownish-black precipitate is allowed to subside, and the supernatant liquid poured through a small filter. Boiling water is added to the residue, and, after subsidence, the liquid is again poured off. This washing is repeated two or three times, when the whole of the precipitate is carefully transferred to the filter, and thoroughly washed with hot water. It is dried, transferred to a crucible, ignited, and weighed. The precipitate of oxide of copper should at first be ignited gently, but afterwards intensely, and weighed as soon as the crucible is cold. The ash of the filter must be ignited separately on the lid of the crucible, and any metallic copper contained therein converted into oxide by addition of a drop or two of nitric acid, careful drying, and ignition. If iron is present in the sample the precipitate will contain ferric oxide, which must be estimated and deducted (see below). 79·4 parts of copper oxide correspond to 63·4 parts of metallic copper, or 249·4 parts of crystallised copper sulphate.

Estimation by Precipitation as Metallic Copper.—About 0·5 grm. of the sample is dissolved in a little water, in a weighed platinum dish. The copper may be deposited electrolytically or by the following process:— Sulphuric acid and a rod of pure zinc are added and the dish covered with a clock-glass. The copper is thereby precipitated on the platinum. When the reaction is complete, which is known by a drop of the liquid producing no brown colour with sulphuretted hydrogen, the zinc is carefully removed, and the dish with the deposit thoroughly washed, dried at 100° C., and weighed. Instead of drying and weighing the metallic copper, it may be dissolved in a mixture of hydrochloric acid and ferric chloride, diluted with water (Fleitmann's method), and the ferrous chloride formed titrated with $\frac{N}{10}$ permanganate. There are many other volumetric processes for estimating copper, descriptions of which may be found in *Sutton's Volumetric Analysis.*

Estimation of Iron.—About 5 grms. of the sample should be taken, dissolved in 100 c.c. of water and boiled with addition of a few drops of nitric acid. The liquid is cooled, diluted to about 300 c.c., and an excess of ammonium hydrate added. The ferric oxide which is thus precipitated is collected on a filter, washed, re-dissolved in hydrochloric acid, and again precipitated by ammonia in the cold. The liquid is filtered, the oxide of iron washed, dried, ignited, and weighed as Fe_2O_3.

COPPER SULPHIDE, CuS, may be prepared by treating sulphate of copper solution with sodium sulphide or sulphuretted hydrogen. It is a black paste when freshly precipitated, and is insoluble in dilute acids and alkalies. It is easily oxidised, hence is best stored in vessels protected from the air and containing a little ammonium sulphide. It is used in the printing and dyeing of aniline black.

COPPER SULPHOCYANIDE or **THIOCYANATE,** $Cu_2(CNS)_2$.—Copper thiocyanate is made by precipitating a solution of copper sulphate containing ferrous sulphate or sulphurous acid, by means of potassium sulphocyanide. The white precipitate which is thrown down is known as *white paste*, and as usually sold contains about 47 per cent. of the pure salt. It is insoluble in water, and is used in the production of aniline black. It is poisonous.

**COPPER SPOTS ON FABRICS** *v.* Textile Fabrics, Analysis of.

COPPERAS *v.* Iron (Ferrous Sulphate).

CORALLIN. *Red corallin, Red aurine, Pæonine.* A triphenyl carbinol derivative prepared by action of ammonia on aurine. Brown powder, insoluble in water.

Application.—*v.* Aurine.

CORCHOROBASTOSE *v.* Jute.

CORÉINE (D. & H.). Produced by action of dimethyl (or ethyl) amidoazobenzol on gallaminic acid.

$$\left(\text{Gallaminic acid} = C_6H_3 \diagdown \genfrac{}{}{0pt}{}{CONH_2}{(OH)_2} \right)$$
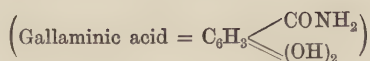
1893. Black powder, giving green solution in water. In concentrated H_2SO_4, blue solution, red on dilution.

Application. — A mordant dye. Dyes chrome-mordanted *wool* or *cotton* blue.

CORËINE A B and A R (D. & H.). Obtained by phenylating and sulphonating corëine. 1894. Dark blue paste soluble in water. In concentrated H_2SO_4, reddish-violet solution, becoming yellow on dilution.

Application.—As CORËINE,

CORËINE R R (D. & H.) *v.* CELESTINE BLUE B (By.).

CORUNDUM *v.* ALUMINIUM OXIDE.

COTTON — *Origin.* — Cotton is the fine woolly fibrous material which is attached to and envelopes the ripe seeds of various species and varieties of the genus *Gossypium*, belonging to the natural order *Malvaceæ*. The actual number of distinct species of cotton plant is a matter of discussion, some botanists being of opinion that there are only four, while others distinguish as many as ten.

In the following list the four possessing indisputable characters are placed first :—

1. GOSSYPIUM BARBADENSE. — This, the most valuable variety, produces the long, silky *Sea Island* cotton. It is largely cultivated in South Carolina, Georgia, Florida, and the West Indies, and grows to a height of 12 to 15 feet. The seeds are smooth, small in size, and black, and the plant produces a yellow flower.

2. GOSSYPIUM PERUVIANUM.—This species is indigenous to several parts of South America, being cultivated principally in Peru and Brazil. The plant attains a height of 10 to 13 feet, and bears a yellow flower. The pods, which usually contain eight to ten black seeds each, yield a long staple, strong and somewhat coarse fibre, which is much esteemed.

3. GOSSYPIUM HERBACEUM.—This variety is sometimes known as *G. Indicum*. It is native in many parts of Asia, and is a small (3 to 4 feet), bushy, very hardy plant, bearing a yellow flower. It is cultivated in India, Egypt, China, and America, in localities where other varieties cannot be satisfactorily grown. It produces a short and relatively coarse fibre, which is commonly known as *Surat* or *Indian* cotton.

4. GOSSYPIUM ARBOREUM.—This, the so-called cotton tree, reaches a height of 20 to 25 feet. It is found in India, Ceylon, China, Arabia, United States, and Canary Islands, and bears reddish-purple flowers. The staple is of good quality.

5. GOSSYPIUM HIRSUTUM.—This is usually classed as a sub-species of *Barbadense*. It grows 6 or 7 feet high, and is the variety from which the bulk of United States cotton is obtained. The flower of this plant, which is cultivated in Siam and Burmah, as well as in the United States, is white or faintly yellow.

6. GOSSYPIUM RELIGIOSUM, or Chinese cotton plant, is one of the few varieties yielding a naturally coloured fibre. It is a small shrub, reaching a height of only 3 or 4 feet, and is grown in China, Siam, India, some of the West Indies, and, to a small extent, in Malta. The fibre is of a yellowish-brown colour, and is frequently known as *Nankin* cotton.

Other varieties are GOSSYPIUM CONGLOMERATUM (Martinique), G. ACUMINATUM (India), G. VITIFOLIUM (Pernambuco), and G. FLAVIDUM (United States).

Samples of cotton from the interior of Africa said to possess a natural yellow, pink, and even crimson colour have been exhibited, but their authenticity has never been established, and is indeed extremely doubtful.

Cotton appears to have been known and used in Persia, India, and Egypt from the remotest times. Herodotus,[*] when writing of India (B.C. 445), mentions "trees bearing a sort of wool instead of fruit, which was finer and better than that of sheep." Its natural growth is very widely distributed, and in all hot countries natives of even the most primitive type are accustomed to its use. Pliny,[†] in his history when dealing with Egypt, mentions a "kind of cloth, *Xylina*, made from wool growing on a shrub, which some call *Xylon* and some *Gossypium*." *Gossypium* is thus probably an Egyptian word, while *Xylon* is abbreviated from *eryxylon* (Gr.), which signifies *tree-wool*.[‡] It is interesting that the German, Danish, Dutch, and Swedish names for cotton also mean "tree-wool." The English, *cotton*, French, *coton*, and Italian, *cotone*, on the other hand, are derived from the Arabian, *cotuna*.

Cotton was probably introduced into Europe by the Saracens, and first manufactured in Spain in the early part of the thirteenth century. The manufacture of cotton cloth was introduced into England by the Dutch,[§] and the first mention of the trade in Lancashire is probably contained in L. Roberts' *Treasury of Traffic*, published in 1641, in which, speaking of Manchester, he says :—" They buy cotton wool in London that comes from Cyprus and Smyrna, and at home work the same and perfect it into velveteens, fustians,

---

[*] *Heroditus*, Bk. iii.   [†] *Pliny*, Bk. xix., chap. v.
[‡] Bancroft, *Philosophy of Permanent Colours*, vol. i. p. 107.
[§] *Manual of Dyeing*, Knecht, Rawson, and Loewenthal, p. 13.

dimities, and other such stuffs, and then return it to London, where the same is vended and sold, and not seldom sent into foreign parts."

Mode of Growth of the Fibre.—The fruit of the cotton tree is a pod or nut of about the size of a filbert, which is divided longitudinally into three, four, or five valves by thin internal membranous ribs. Each of these valves contains three or more seeds, surrounded, in the early stages of growth, by a mass of pulp or milky fluid. The fibres make their appearance upon the seed at an early period, and as they gradually develop, the pod becomes filled with an intricate mass of fibres, the growth of which eventually bursts it open.

When this occurs, the exposure to sun and air causes a rapid disentanglement and development of the still pulpy and more or less cylindrical fibres, which soon become consolidated and dried, consequently losing their cylindrical or tubular form, and appearing as flattened band-like threads, still, of course, attached to the seed at their inner extremity. At this stage the seed pod, which is now termed a *boll*, has the appearance of a white fluffy ball of fibre; and when completely ripe, these bolls are picked off by hand and the seed separated from the fibre by a process termed *ginning*.

The cotton seeds are submitted to hydraulic pressure and yield *cottonseed oil*, which is used for the manufacture of soap, &c., and the ginned cotton forms the raw material for the manufacture of cotton cloth.

Physical Structure of the Fibre.—A cotton fibre, when examined microscopically, appears as a long and relatively narrow, flattened tube, spirally twisted about its axis. It is, indeed, an enormously elongated, compound plant cell, one end of which is pointed and closed, and the other—that by means of which the fibre was attached to the seed—is irregularly torn. There is, however, much individuality amongst cotton fibres, no two being precisely similar in appearance.

The variations are still more marked when cross-sections of various fibres are examined, some exhibiting thick cell walls with a very small central cavity, while in others the hollow tubular space is greatly enlarged. Certain fibres also retain much of their original cylindrical form, while others are completely flattened and exhibit a mere line instead of a central cavity.

One abnormal condition of the fibre is extremely common. In this the cell takes the form of a ribbon or band, the tubular form having never been developed. Such fibres, which are termed "dead" or "unripe" cotton, appear as thin, irregularly bent, flat rods. Dead cotton is very difficult to dye, and frequently appears as white specks on dyed pieces, particularly in such as are dyed indigo-blue or Turkey red.

The length of staple and diameter of various cotton fibres vary greatly, as will be seen from the following table,[*] which also conveniently serves to indicate the chief commercial varieties :—

LENGTH OF STAPLE AND DIAMETER OF COTTON FIBRES.

	Length. mm.	Diameter. mm. $\frac{}{1000}$
(a) North American Varieties—		
Sea Island (Georgia), .	28 to 36	14
Louisiana, . .	20 ,, 26	17
Alabama, . .	18 ,, 25	17
Florida, . .	18 ,, 25	18
Upland (Georgia), .	17 ,, 25	19
New Orleans, . .	17 ,, 25	19
Tennessee, . . .	17 ,, 25	19
(b) Central and North American Varieties—		
Pernambuco (Brazil), .	30 to 38	19
Ceara (,,),	23 ,, 30	21
Bahia (,,),	27 ,, 36	18
Maragrau (,,),	23 ,, 30	..
Surinam (Guiana), .	25 ,, 30	..
Demerara, . .	23 ,, 32	19
Berbice (Guiana),	20 ,, 29	..
Barcelona (,,),	20 ,, 36	19
Cartagena (,,),	20 ,, 27	..
Lima (Peru), . .	23 ,, 29	..
Hayti (West Indies), .	21 ,, 28	15
Porto Rico (,,),	21 ,, 28	..
Guatemala (,,),	25 ,, 21	15
Cuba (,,),	21 ,, 28	..
(c) Asiatic Varieties—		
Surat, . . .	20 to 26	20
Madras, . . .	20 ,, 26	28
Bengal, . . .	13 ,, 22	20
Persian, . . .	18 ,, 25	23
Nankin, . . .	..	25 to 40
(d) African Varieties—		
Egyptian, . . .	27 to 36	15
Bourbon, . .	20 ,, 27	15
(e) Levant Varieties—		
Smyrna, . . .	16 to 20	24
Macedonia (Turkey), .	15 ,, 20	24
(f) European Varieties—		
Spanish, . . .	20 to 30	17
Italian, . . .	18 ,, 22	19

Expressed in inches, the length of cotton fibre varies from 0·8 to 1·8 inch, and the diameter from 0·0005 to 0·001 of an inch. The length is thus from one thousand to two thousand times the diameter, and if a fibre was magnified to the thickness of an ordinary lead pencil, its length would be 8 to 15 yards. As a rule, as will be seen in the above table, the longest fibres have the smallest diameter.

[*] Abstracted from Hoanel's *Mikroskopie der Faserstoffe.*

Under certain conditions, but not invariably, the cotton fibre is surrounded by an extremely thin membrane, termed the *cuticula*, which envelopes or is wound round it spirally. During the bleaching process, however, this is removed, or, at anyrate, modified in such a manner that it cannot afterwards be distinguished from the rest of the fibre.

Physical Properties of Cotton.—Under this heading we may distinguish (1) *Strength*, (2) *Spinning Property*, (3) *Capillarity*.

(1) *Strength.*—The breaking strain of the fibre varies pretty regularly with the diameter, the coarser varieties being stronger than the finer sorts. The breaking strain of a single fibre varies from 80 to about 160 grains (= 5 to 10 grams). Comparing silk, wool, and cotton fibres of equal diameter, silk is much the strongest fibre, wool the weakest, while cotton holds an intermediate place. In respect of elasticity, apart from that due to the spiral character of the fibre, both wool and silk are, however, much superior to cotton.

(2) *The spinning property* of cotton, which renders it possible to produce from this fibre an extremely fine thread, is largely dependent upon its spiral character, this greatly facilitating the interlocking of the fibres and largely increasing their grip upon one another. According to Bowman, never more than 30 per cent. of the ultimate strength of the fibres is utilised in the spun yarn, the thread always breaking by the drawing out of fibres from their places in the yarn before that limit is reached. In the woven cloth, however, the thread would be subject to much greater compression ; and since the friction of the individual fibres would therefore be much increased, the strength of the thread would in all probability approximate much more nearly to the sum of that of its ultimate fibres. The spiral character of the fibre is due to unequal or irregular drying of the walls.

(3) The very considerable *capillary* attraction exerted by the fibre is due to its tubular structure, and to the fact that the cell walls, where at all thick, separate during the drying of the fibre substance into several layers, between each pair of which there is a minute cavity.

CHEMICAL CONSTITUTION OF COTTON.

Under the chemical and physical influence of sunshine, living plants possess the property of abstracting from the atmosphere the carbon, hydrogen, and oxygen required for their nutrition, deriving these elements from the carbon dioxide and the aqueous vapour always present in the air. It is not unlikely that the first stages of the process consist in the formation of comparatively simple but highly unstable substances, which, probably by a process of condensation, gradually increase in complexity and stability until eventually a stable substance, cellulose, is formed. Chemical processes then yield to physical ones. The cellulose assumes a definitely organised structure and constitutes the woody framework of the plant growth.

Cellulose $(C_6H_{10}O_5)x.$—This is the chief product of vegetable life, being an essential constituent of plants, and forming the larger proportion of their mass. The sources of cellulose are very extensive, and furnish an enormous supply of raw material for industrial substances. Although so abundant, it is, however, never found in a pure condition, being usually associated with other organic products, mainly of the nature of starches, acidic and astringent substances, resins, gums, &c., which constitute the rest of the plant. Cellulose may thus be looked upon as the plant skeleton.

The purest natural form of cellulose is *cotton fibre*, which in the raw material contains about 5 per cent. of impurity. Other vegetable fibres, such as *linen, hemp, jute, China grass*, &c., are naturally associated with from 30 to 70 per cent. of extraneous matter, from which they can only be separated with difficulty. The amount of cellulose in *wood* is very variable; in young green wood it may be 30 to 40 per cent. only, while in older dry wood it may reach 80 to 90 per cent.

Strictly speaking, the structural portion of all plants is not identical, and the cellulose of the cotton fibre is only one member of the "cellulose group." The celluloses which are employed as sources of textile fabrics are designated "fibres," in distinction to those "fibrous substances" which can only be used in the manufacture of paper, &c.

Physiologically, cotton fibre is distinct from other celluloses. It consists, as already mentioned, of the enormously elongated compound plant cells which surround the seeds of *Gossypium Barbadense* and other species, and merely requires to be separated from the seeds before use as a textile fibre.

The fibres of other plants are classified as *exogenous* and *endogenous*, according to the mode of growth. In *exogens* the fibrous portion constitutes a distinct layer between the central woody portion and the bark— *e.g.*, *flax, China grass ;* while in *endogenous* plants (*e.g.*, *jute*) the fibrous cells aggregate into bundles, termed *fibro-vascular bundles*, which are scattered throughout the whole of the stem or leaf, as the case may be. When the fibro-vascular bundles are not arranged more or less parallel to one another, but are crossed or interlaced, the fibre cannot be separated as a textile raw material, but is suitable only for yielding the fibrous pulp from which paper is made.

It is generally considered that at any rate a portion of the impurities with which celluloses are always associated is in a state of chemical combination with the cellulose, and this results in a great difference in the chemical behaviour of cellulose raw materials, termed *compound celluloses*. These may be classified into *adipo-celluloses*, *pecto-celluloses*, and *ligno-celluloses*, according to the nature of the associated substances.

Adipo-celluloses constitute the protective covering of plants, and are of a cellular, and not a fibrous character. These bodies are much richer in carbon and poorer in oxygen than cotton cellulose, Cross and Bevan giving the composition as C 73·06, H 11·37, O 14·97.

The chief adipo-celluloses are cork and bark. These always contain a number of impurities—viz., tannins, wax, and proteids—which may be removed by the aid of solvents, leaving as a residue a body, *cutose*, which is of the composition given above. Under suitable treatment, cutose is decomposed into cellulose, and a wax-like body of unknown composition. With the exception of cotton, all cellulose fibres contain more or less adipo-cellulose, which has to be removed during the bleaching operation. The long operation required in the bleaching of linen is due mainly to the great difficulty of resolving the adipo-cellulose into cellulose and wax, and removing the latter substance without attacking the valuable fibre.

The group of *pecto-celluloses* include most of the vegetable fibres, excluding *cotton*, which forms a class to itself; and jute, which belongs to the ligno-celluloses. The non-cellulose constituents in this case are pectic substances, these being a class of vegetable extractive bodies of an acid character, and giving solutions which readily gelatinise. Unlike the adipo-celluloses, they are slightly richer in oxygen than cellulose itself, an analysis of raw flax, which is typical of this class, giving C 43·7, H 5·9, O 50·4. On boiling with dilute alkali the pecto-celluloses are readily resolved into cellulose, the pectic matters being converted into soluble derivatives, and this takes place during the bleaching of linen, &c.

The *ligno-celluloses* include the woody portion of trees and many leaves, &c., as well as one textile fibre, *jute*. Raw jute is richer in carbon than cellulose.

The following table indicates the relative composition of the celluloses :—

				Cellulose.	Adipo-cellulose.
Carbon,	.	.	.	44·1	73·6
Hydrogen	.	.	.	6·3	11·4
Oxygen	.	.	.	49·6	15·0

				Pecto-cellulose.	Ligno-cellulose.
Carbon,	.	.	.	43·7	47 to 48
Hydrogen,	.	.	.	5·9	5·9 ,, 5·5
Oxygen,	.	.	.	50·4	47·1 ,, 46·3

Ligno-cellulose is of a much more active chemical nature than cellulose itself. It is readily attacked by acids, alkalies, oxidising and reducing agents, &c., in some cases cellulose being separated, whilst in others soluble products are found. The chemistry of the ligno-celluloses is of the greatest importance in connection with paper manufacture, but is of little interest from the point of view of the textile trades, except as regards the dyeing of jute. According to Sachsse, ligno-cellulose consists of about 75 per cent. cellulose and 25 per cent. *lignin*, a body of an aldehydic character.

As already mentioned, *cellulose* has the composition C 44·1, H 6·3, O 49·6, which corresponds to the empirical formula $C_6H_{10}O_5$, but its molecular weight is certainly greater than is represented by this formula, the cellulose molecule probably containing 24 or 36 carbon atoms. Its exact constitution is unknown, but from a consideration of its reactions Cross and Bevan have applied to the unit or C_6 group the formula :—

$$\begin{array}{c} \lceil\!\!-\!\!-\text{O}\!\!-\!\!-\!\!\rceil \\ -\text{CH}\,.\,\text{CH}\,.\,\text{OH}\,.\,\text{CH}\,.\,\text{CH}\,.\,\text{OH}\,.\,\text{CH}\,.\,\text{OH}\,.\,\text{CH}_2- \\ \lfloor\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-\text{O}\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-\!\!\rfloor \end{array}$$
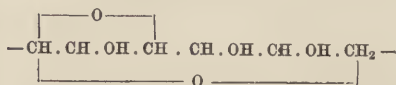
When cellulose is heated with acetic anhydride it yields a deca-acetate, $C_{12}H_{10}(C_2H_3O_2)_{10}$. It therefore contains ten hydroxyl groups in the molecule C_{12}, and may conveniently be expressed as $(C_{12}H_{10}(OH)_{10})x$. Cellulose is a very inert substance, having neither acidic nor basic properties. It is devoid of taste or smell, is colourless, more or less opaque, and has a density of 1·2 to 1·45 (water = 1). It is quite insoluble in water, alcohol, ether, and all common solvents, and is unaffected by dilute acids and alkalies. Under suitable conditions—which will be referred to later—it may be hydrated, in which condition it forms a gelatinous mass, being thus a typical *colloid*.

Cellulose dissolves readily in an ammoniacal solution of oxide of copper (Schweizer's reagent), which is best prepared by dissolving copper filings in ammonia by passing a current of air or oxygen through the liquid. The ammoniacal solution of the precipitated hydrate has much less solvent action on cellulose. When treated with this reagent, cellulose swells up, becomes gelatinous, and finally completely dissolves. From this solu-

tion cellulose is reprecipitated by acids or slowly by dilution, forming a gelatinous mass. Neutral salts precipitate a blue compound containing copper oxide, which is, however, readily dissolved by ammonia. It has recently been shown that some oxycellulose is formed during the solution of cellulose in Schweizer's reagent. If instead of effecting complete solution of the cellulose, the action of the ammonio-copper solution is confined to the surface of the fibre, a fabric is formed, which is both waterproof and rot-proof. An important industrial application of the process occurs in the manufacture of so-called "WILLESDEN CANVAS," which is formed by passing the woven material through the copper solution, and thence to drying cylinders, when each fibre is superficially acted upon and becomes coated with a gummy layer of the viscous oxycellulose in combination with copper oxide. On drying, this "welds" the whole fabric together, the oxycellulose film imparting waterproof, and the copper antiseptic properties. If two or more sheets are passed together through heavy rollers during the action of the solution, they are permanently welded into one coherent fabric. "Willesden canvas" possesses a green colour, due to the presence of the copper. It is employed for making sails, tents, cart-covers, &c., &c. Cordage is also treated in a similar manner.

Another good solvent for cellulose is a solution of fused chloride of zinc (1 part) in strong hydrochloric acid (2 parts), which dissolves it almost instantly without sensible change.

CHEMICAL REACTIONS OF CELLULOSE AND THE PRODUCTS THEREBY OBTAINED.

Action of Heat.—When gradually heated, cellulose first parts with its hygroscopic moisture, and then, at about 250° C. begins to turn brown. In the presence of air it then ignites and burns with a luminous flame and almost without smell; but, if damp, it smoulders, and gives off the irritating fumes of acrolein. If heated to a high temperature without access of air (dry distillation) it is partially resolved into gaseous products, leaving a residue of carbon. The volatile products are numerous, but those of chief importance are *acetic acid*, *acetone*, *methyl alcohol*, and *wood tar*, the latter containing the hydrocarbons *xylene*, *chrysene*, *naphthalene*, *anthracene*, and the higher members of the paraffin series.

Action of Acids.—When cellulose is immersed in a dilute solution of mineral acid a certain degree of concentration of acid upon the fibre takes place, but the effect is too slight to be of much technical importance.

With strong acids, however, more important results follow.

Sulphuric Acid.—If cellulose is steeped in concentrated sulphuric acid it swells up to a gelatinous mass, and if, at this stage, it is diluted with water, a precipitate is obtained of a modified cellulose, termed *amyloid*. If the cellulose is in the form of absorbent paper, and the action is superficial only, the paper is rendered grease-proof, and its strength is increased three or four-fold. Such paper, which is known as *vegetable parchment*, is made by immersing suitable unsized paper in sulphuric acid at 135° Tw. for ten seconds, and at once washing and drying.

If the action of the acid is allowed to continue for one or two minutes, the cellulose completely dissolves, and is converted into a gum-like substance, *dextrin*, which may be obtained by neutralising the liquid with chalk, filtering off calcium sulphate and excess of chalk, and evaporating the solution to dryness. Dextrin has the same percentage composition as cellulose, $C_6H_{10}O_5$, but the molecule is probably less complex than that of cellulose.

If, instead of neutralising the acid solution, it is diluted and boiled, the dextrin is converted into dextrose, commonly known as *glucose* or *grape sugar*. The constitution of this body has been determined, and is represented as follows:—

$$CH_2 . (OH) . (CH . OH)_4 . CHO.$$

It thus belongs to the aldose group of monosaccharoses.

The use of amyloid as vegetable parchment has been alluded to. It is prepared from paper-cellulose. Dextrin is, however, usually made from starch, and not from cellulose. It is extensively employed as a thickening agent in *calico* printing and other processes, and is also applied as an adhesive to postage stamps, gummed labels, &c. It is not such a permanent adhesive as true gum, from which it may be distinguished by its sweetish taste, gum arabic or other gums having a slightly acid taste. Labels attached with dextrin frequently fall off in a damp atmosphere.

Dextrose, like dextrin, is usually prepared from starch or wood. It is a sweetening material, and is used in enormous quantities as a substitute for sugar in the manufacture of cheap jams, sweetmeats, &c., and in the manufacture of alcohol.

The Carbonising Process.—When boiled in dilute sulphuric acid, or when steeped in dilute acid and dried, the cotton fibre is tendered, rotted, or even entirely disintegrated, quite losing its fibrous character, and falling to dust when rubbed or shaken.

This forms the basis of the *carbonising* or *extracting* process, the object of which is to remove any cotton fibre or other vegetable

matter which may be present in wool fabrics. There are two methods of conducting the process, known respectively as "wet carbonising" and "dry" or "gas" carbonising. In the wet process the material is steeped in a solution of sulphuric acid at about 4° Tw. until saturated, then hydro-extracted and dried, first at a temperature of 40° C., and afterwards at 70 to 80° C., after which the vegetable matter, which crumbles to dust, is mechanically removed. This process is applied to certain kinds of woollen cloth and to felt-hat bodies.

The "dry" process, which is chiefly employed in the carbonising of "shoddy," "mungo," or "rags," is conducted by exposing the material to the action of dry hydrochloric acid gas at a temperature of 100° C. Solutions of many metallic salts, if concentrated, have a similar destructive action on cotton, and it is therefore essential that after treatment with solutions of acids or metallic salts for any purpose, the cotton should be well washed, since if allowed to dry the solutions concentrate upon the fibre and rot it.

The powdery disintegrated fibre substance consists of hydrocellulose, $(C_{12}H_{22}O_{11})x$.

Nitric Acid.—Many interesting and commercially valuable products are produced by the action of nitric acid on cellulose under varying conditions, or from raw materials obtained thereby, and amongst these may be mentioned *collodion, gun-cotton, vulcanite, artificial silk,* and *oxalic acid.* Boiling concentrated nitric acid converts cellulose into *oxalic acid* and *beta-oxycellulose,* an amorphous substance which forms a gelatinous hydrate with water and is easily soluble in alkalies. It also dissolves in sulphuric acid, yielding a pink solution. Beta-oxycellulose has no technical importance.

Cold nitric acid, or a mixture of nitric and sulphuric acids, or sulphuric acid and a nitrate give, on the other hand, nitrated products, which are usually termed *nitro-celluloses;* but as they are true ethereal salts, they are more correctly termed *cellulose nitrates.*

The action of nitric acid on starch (which is closely allied to cellulose) was first investigated in 1833 by Braconnot, who noticed that a very inflammable body was produced, which he termed *xyloidine.* *Gun-cotton* was discovered in 1846 independently by Schönbein, Bottger, and Otto, the credit being usually ascribed to the first-mentioned chemist.

There are a number of different cellulose nitrates, the degree of nitration depending upon the strength of the acid, the length of time the action is allowed to continue, the temperature, and the physical condition of the cellulose. It is, however, difficult to produce any particular nitrate in a pure condition, or to isolate the various members of

the series. The *di, tri, tetra, penta,* and *hexa-nitrates* are all known.

Cellulose dinitrate, $C_{12}H_{18}(NO_3)_2O_{10}$, is the principal product of the action of hot dilute nitric acid on cotton. It is also produced by treating the higher nitrates with dilute alkali, but concentrated alkalies split up the molecule with production of tarry matters. Cellulose dinitrate is soluble in absolute alcohol or alcohol-ether (a mixture of alcohol and ether). It is not explosive, but is more inflammable than ordinary cotton.

A mixture of the *tri-* and *tetra-nitrates,* $C_{12}H_{17}(NO_3)_3O_{10}$ and $C_{12}H_{16}(NO_3)_4O_{10}$, is known as *collodion pyroxylin* or *soluble pyroxylin.* A solution of this in alcohol-ether is known as *collodion,* and is a colourless, viscous liquid, which dries to a thin, lustrous, pliable film, insoluble in water. It is used extensively in photography, and in surgery as a varnish to exclude the air from wounds. It is from this nitrated product that "artificial silk" is prepared (*v.* SILK, ARTIFICIAL).

Cellulose penta-nitrate, $C_{12}H_{15}(NO_3)_5O_{10}$, is best produced by dissolving the hexa-nitrate in nitric acid and precipitating by sulphuric acid. It is slightly soluble in alcohol-ether.

Cellulose hexa-nitrate, $C_{12}H_{14}(NO_3)_6O_{10}$, constitutes ordinary *gun-cotton.* It is the most highly nitrated cellulose known, and is formed by steeping cotton for twenty-four hours at a temperature not exceeding 10° C. in a mixture of 1 part concentrated nitric acid and 3 parts concentrated sulphuric acid. It is insoluble in alcohol, ether, or their mixture, but is slightly soluble in acetone. The body is extremely inflammable, but burns quietly if ignited in the air. If ignited in a closed space it is highly explosive. *Blasting gelatine* consists of gun-cotton impregnated with nitro-glycerine.

The higher members of the series are all converted into the dinitrate by treatment with dilute alkalies, and are partially denitrated by boiling with dilute nitric acid. In the manufacture of "artificial silk" ammonium sulphide is sometimes employed as a denitrating agent.

The physical appearance of the cellulose is little affected by the nitrating process, but its chemical properties are materially altered. The nitrates are all insoluble in water; their solubility in alcohol or ether diminishes, but their inflammability increases as the series ascends. The affinity of the cellulose nitrates for dyes is much greater than that of cellulose itself, but this property is of no technical value.

ORGANIC ACIDS, as might be expected, exert much less injurious action on cotton than mineral acids.

Acetic acid, probably on account of its volatility, appears to be quite harmless under any

condition of practical work,[*] but with this exception all the common organic acids effect a greater or less tendering action upon the fibre, especially when dried at a high temperature. The action is, at anyrate partially, mechanical, the acid crystallising in the interior of the fibre and thus causing a rupture of the cell walls. Oxalic acid is much the most destructive, while citric acid has much less action than tartaric acid. In all cases a dry heat is much more injurious than the moist heat of a steaming-box at the same temperature, and this point should be kept in view in calico printing processes. Solutions of most organic acids, unless excessively concentrated, have no action upon cotton even at a boiling temperature, but if the fibre is saturated with a solution containing even as little as 5 grms. oxalic acid per litre, and subsequently dried at 100° C., it is practically disintegrated.

Cellulose does not appear to exert any selective affinity or attraction for the above-mentioned organic acids, but towards tannic acid it behaves differently, readily withdrawing it from solution ; and upon this fact the use of tannin matters in cotton dyeing processes is based. (*v.* TANNIC ACID.)

Action of Alkalies.—Solutions of *alkaline carbonates*, *soap*, or *ammonia* have no action on cellulose, even at a temperature considerably over 100° C. ; but at 200° C. ammonia enters into combination with the cellulose molecule, and the nitrogenous product thus obtained behaves towards dyes in a manner similar to the animal fibres. This process, due to Vignon, thus serves as a means of "animalising" cotton.

The action of solutions of *caustic alkali* depends upon their concentration and temperature. Solutions containing 2 to 3 per cent. Na O H have little action up to a temperature of 150° C. ; in fact, one of the chief processes in bleaching cotton consists in its treatment with boiling caustic alkali, which, while attacking most of the impurities, has no effect on the fibre substance itself. If the boiling takes place in an open vessel, and the material is not completely covered by the solution, a somewhat rapid tendering or rotting of the cotton takes place, this being due to oxidation of the cellulose, induced by the simultaneous action of air and caustic alkali. According to C. O. Weber,[†] caustic potash has a much greater destructive action than caustic soda.

The ultimate product of the oxidation of cellulose in alkaline solution is *oxalic acid*,

which body is commercially prepared by means of this reaction. Malic acid is also produced as an intermediate product.

At elevated temperatures a 4 per cent. solution of NaOH slowly converts cellulose into soluble products, the action increasing with the temperature as follows (H. Tauss[*]) :—

Steam Pressure.	Cellulose Converted into Soluble Products.
15 lbs.	12·1 per cent.
75 ,,	15·4 ,,
150 ,,	20·3 ,,

With an 8 per cent. solution of caustic soda, the percentage of soluble products is increased nearly threefold.

MERCERISATION.

Cold concentrated solutions of caustic alkali affect cellulose in a remarkable manner. If steeped in a solution containing upwards of 20 per cent. of NaOH (= 45° Tw.), the structural appearance of the cotton fibre is greatly modified, changing from that of a flattened spiral tube, with thin walls and a relatively large central cavity, to a straight, more or less cylindrical tube, with thick walls and a greatly diminished central cavity. The effect of this modification of the fibre, in mass, is that cotton cloth thus treated contracts in length and breadth, becoming at the same time translucent, thicker in substance and much stronger.

This curious effect is due to the formation of a definite chemical compound, $(C_6H_{10}O_5 + NaOH)_x$, in a state of hydration. By treatment with water the alkali is removed and cellulose regenerated, not, however, in its original form, but as a hydrate, $(C_6H_{10}O_5 . H_2O)_x$. which permanently retains its characteristic appearance and properties.

The peculiar effect above described was first noticed and investigated by Mercer (1844), who patented the process ; and although it aroused a good deal of interest at the time, and was exhibited at the first international exhibition (London, 1851), very little practical use was made of the process until recently. It is, however, now in extensive use for the production of *crepe* and *crepon* effects on cotton or mixed goods.

The degree of contraction brought about by the mercerising process varies with the character of the material and the intensity of the action, from one-fifteenth to one-fifth of the total length and breadth of the cloth. The strength of the material is increased in an even greater degree, the relative breaking

* When heated with acetic anhydride in a sealed tube to a high temperature, cellulose acetates are formed, the ultimate product being the deca-acetate, $(C_{12}H_{10}(C_2H_3O_2)_{10})_x$.

† *Journ. Soc. Chem. Ind.*, 1893, p. 118.

* *Journ. Soc. Chem. Ind.*, 1889, p. 913 ; 1890, p. 883.

strain before and after treatment being as 12 to 22 or 24. The permanent increase in weight, due to hydration, is between 4·5 and 5·5 per cent.

Another notable change brought about by the mercerising process is that the fibre acquires a greatly increased affinity for most colouring matters, the effect being particularly well marked in the case of the direct cotton colours, and also with Turkey red.

"Mercerisation" may also be brought about by substances other than caustic alkali—e.g., sulphuric, nitric, or phosphoric acid or zinc chloride, the use of these bodies being included in Mercer's patent specification.[*]

The Lustreing of Cotton.—This is now the most important application of the mercerising process, the effect being brought about by mechanically preventing the contraction which normally occurs during the treatment with caustic soda. The process was first brought prominently before the public by the patent of Thomas and Prevost in 1896. The importance of the process has developed at an enormously rapid rate, and the literature of the matter is too voluminous to be here summarised. The most important improvements have been in relation to the methods of applying the necessary tension, and no essential advance has been made in respect of the chemical side of the process. Lustred cotton almost rivals silk in appearance, but its lack of elasticity causes fabrics made from it to quickly crease. The maximum degree of lustre can only be produced on Sea Island or Egyptian cotton.

Cellulose Thiocarbonates.

These substances, discovered by Cross, Bevan, and Beadle in 1893,[†] promise to become of great technical and commercial importance.

When mercerised cotton is exposed to the action of carbon disulphide at the ordinary temperature, a reaction occurs with production of an alkali-cellulose-xanthate of the type—

$$CS{<}^{O\,(C_6\,H_{10}\,O_5)}_{S\,Na}.$$
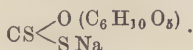
In carrying out the process, bleached cotton is treated with excess of NaOH 50° Tw., and squeezed until it retains about three times its weight of the solution. It is then placed in a closed vessel, and carbon disulphide to the extent of 40 per cent. of the original weight of cotton, is added. After standing for three hours the mass is covered with water and allowed to stand several hours

* An extremely interesting account of Mercer's researches on this and other points will be found in *The Life and Labours of John Mercer*, by E. A. Parnell. London, 1886.

† *Proc. Chem. Soc.* (London), 1893, p. 108.

longer, when, on agitation, a homogeneous liquid of extraordinary viscosity is obtained, which may be diluted with any extent with water.

The crude product thus obtained is of a yellow colour, and may be purified by precipitating its aqueous solution with salt or alcohol. It then forms a greenish-white flocculent mass, which re-dissolves in water to a colourless solution. It is termed *viscose*.

Aqueous solutions of cellulose thiocarbonate slowly undergo spontaneous decomposition, cellulose, caustic soda, and carbon bisulphide being regenerated. The coagulum of cellulose thus reproduced is very gelatinous, the presence of as little as 1 per cent. of cellulose in the original solution being sufficient to form a jelly.

Freshly prepared solutions of the thiocarbonate may be evaporated to dryness at a low temperature without decomposition, but at a temperature of 80° to 90° coagulation rapidly occurs. If dried in thin layers the cellulose is obtained as a homogeneous, colourless, transparent film of great tenacity and considerable elasticity, and of course absolutely insoluble in water. The discovery, which is covered by patents, is probably only in its infancy as regards practical utility, but the product has already been applied as an adhesive substance, as a sizing or filling material for cotton cloth in the manufacture of leather substitutes, for the purpose of producing casts or moulds, and in the production of artificial silk. In bulk the regenerated cellulose forms a transparent mass resembling horn, which can be cut or turned in a lathe, and is capable of taking a brilliant polish. In this form it is an excellent substitute for celluloid, vulcanite, &c.

Oxycellulose.

Under ordinary conditions cellulose resists the action of oxidising agents to a very considerable degree. It is, for instance, quite unaffected by atmospheric oxygen, and only acted upon by such powerful agents as calcium hypochlorite when the solution is of considerable concentration.

On the other hand, the cellulose molecule is profoundly modified by strong oxidising agents, with production first of oxidation products, and finally of decomposition products.

The oxidation may take place in either acid or alkaline solution, and various oxycelluloses are formed according to the conditions which obtain.

Oxidation by Hypochlorite Solution.—Calcium hypochlorite (bleaching powder) is the chief oxidising agent to consider, since this substance is universally employed in the bleaching of cotton. In cold solutions of a

strength not greater than 1° Tw. bleaching powder has no action on cellulose, but a destructive action upon the impurities naturally present upon cotton ; hence its value as a bleaching agent. If, however, the solution is stronger, or if it is used warm or allowed to concentrate upon the fibre, the cellulose itself is attacked and certain defects due to the production of oxycellulose ensue.

These defects, which are usually localised in spots, blotches, or streaks, may render themselves evident by the increased or diminished attraction which such portions of the fabric exert towards different colouring matters, or by the partial or complete disintegration of the portions affected.

This effect is well shown if cotton is spotted with bleaching powder solution about 4° Tw. and then exposed to the air for an hour.

The composition of oxycellulose is probably $C_6H_{10}O_6$ (Nastjukow), but the oxidised fibre probably consists of a mixture of this substance with hydrocellulose ($C_{12}H_{22}O_{11}$) and unchanged cellulose (Cross and Bevan).

Towards colouring matters it behaves in a selective manner, having a marked attraction for *basic* colours, such as methylene blue and methyl violet, but an equally strong repellent action towards the *direct dyeing cotton colours*—e.g., diamine blue or benzopurpurin. The production of oxycellulose has, however, no technical importance as an aid to dyeing processes, because the strength of the fibre is considerably diminished thereby.

The accidental production of oxycellulose by bleaching powder is, as already mentioned, a frequent cause of defects.

Oxycellulose is easily soluble in alkalies, and on this account cotton on which oxycellulose has been produced is greatly tendered by treatment with soap or carbonate of soda solution.

Permanganate of potash in neutral solution has little effect upon cellulose, but in alkaline solution it rapidly attacks cotton, with production of oxycellulose. On treatment with acid oxidising agents, such as nitric acid, chromic acid, &c., oxycelluloses are also formed.

The reactions have little technical interest, but account for the rotting or disintegration of the fibre under certain conditions—e.g., in the production of a discharge pattern by means of chromic acid, upon indigo dyed cotton, and in certain aniline black processes.

Action of Reducing Agents.

Reducing agents, as such, have practically no effect upon cellulose, but if used in acid solution are apt to tender cotton by reason of the acid present. This danger should not be forgotten when discharging colours by means of acid reducing agents, such as a mixture of tin crystals and oxalic acid. Alkaline reducing agents—e.g., a mixture of zinc powder and ammonia—have no action.

Action of Mordants.

Unlike wool, the cotton fibre possesses little power of decomposing metallic salts, such as alum or copper sulphate, this being no doubt due to the fact that cellulose has little affinity for most acids. That a certain degree of attraction does exist is, however, evident from the fact that a solution of a metallic salt, if sufficiently basic, is decomposed by cotton, and the hydroxide or a still more basic insoluble salt is loosely fixed upon the fibre. The action is, however, of small value as a mordanting process, although basic salts are often employed in conjunction with tannic and oleic acids and in other ways.

Certain metallic hydroxides, which can be obtained in alkaline solution—e.g., those of chromium, aluminium, and ferric iron—are distinctly attracted from such solutions by the cotton fibre, the action being sufficiently marked to render this a satisfactory mordanting process. Some few salts, such as chromate of chromium, appear to be attracted even from an acid solution.

The only mordant for which cotton exerts a powerful affinity is *tannic acid*, and this substance is used in enormous quantities in cotton dyeing, both as a mordant and as a fixing agent.

Action of Colouring Matters.

Very few of the natural dyestuffs are capable of dyeing cotton directly—*i.e.*, without the intervention of a mordant—only *turmeric, barberry bark, safflower*, and *annatto* possessing this property. Other natural dyes, such as *catechu, logwood, fustic*, &c., are attracted to a certain extent by cotton, the effect being largely, if not entirely, due to the tannin which they contain. Amongst the artificial dyes the class of so-called *direct* or *Congo* colours are pre-eminent as cotton dyes on account of their great affinity for cellulose; in fact, the introduction of this group of colouring matters has very greatly simplified and very largely revolutionised the art of cotton dyeing.

Other classes of dyes, such as the basic colours, have also a certain affinity for cellulose, and pale shades may be dyed with these colours in a "direct" manner.

The affinity between the direct cotton colours and cellulose is, without doubt, a chemical one; and although cellulose is, in chemical behaviour, very inert, there is probably a chemical action between cotton fibre and colouring matter in most cases of dyeing. For instance, *nitro cellulose* (gun - cotton),

although physically identical with the original cotton, has a much greater affinity for dyes. Oxycellulose also was shown by Witz to have an increased attraction for basic dyes, but a greatly decreased attraction for acid colours. The direct cotton colours also dye oxycellulose much less readily than cellulose itself.

IMPURITIES IN RAW COTTON.

Although cotton fibre is by far the purest form of cellulose, it does not consist entirely of cellulose, but contains, in addition to moisture, about 5 per cent. of foreign matter, the removal of which is the object of the bleaching process.

When freshly gathered a sample of cotton contains a certain amount of oily matter, probably identical with, or closely allied to, the *cottonseed oil* which is obtained from the seeds by pressure. On storage, however, this oil gradually dries up with production of a fatty acid and a waxy mass, termed by Schunck, its discoverer and investigator, *cotton wax*. This wax closely resembles that obtained from the leaves of the Carnauba palm. It is a white, translucent, and friable solid, which melts at 86° C. It is insoluble in water or alkalies, but dissolves easily in alcohol and ether.

This cotton wax, although present in very small amount, is of considerable technical importance. The great difficulty experienced in wetting out raw cotton is probably due to the fact that each fibre is coated with a thin varnish of this substance, and the explanation of the necessity of an elevated temperature in spinning fine yarns is probably that the wax and other impurities require to be softened by heat in order that the fibres may more readily adapt themselves to the new conditions.

Schunck found that the *fatty acid* present is identical in composition with *margaric acid* $(C_{17}H_{34}O_2)$—*i.e.*, with a mixture of stearic and palmitic acids.

The fatty acid is, of course, insoluble in water, but forms a soluble compound (soap) on treatment with alkali. It melts at about 65° C.

Traces of two organic *colouring matters*, to the presence of which in somewhat larger amount the deeper yellow or buff colour of Nankeen cotton is probably due, were also isolated by Schunck.

The bulk of the impurities, however, consist of so-called *pectic acid*, which is probably a compound substance. When purified this forms a pale yellow, amorphous, horny mass, which is soluble in water and has feeble acid properties. Pectic acid does not, however, appear to exist in raw cotton as such, because very little of the impurity is removed by

boiling water. On boiling with dilute alkali, however, a dark brown solution is obtained, which contains the pectic acid along with most of the other impurities.

COTTON BLUE *v.* SOLUBLE BLUE.

COTTON BLUE. Many of the direct cotton blues, such as *Diamine blues*, *Benzo blues*, *Congo blues*, &c., frequently appear under this name.

COTTON BLUE (D.) *v.* BAVARIAN BLUE D B F (Ber.).

COTTON BLUE R (B.) *v.* NEW BLUE (C.).

COTTON BORDEAUX (B.). A tetrazo compound.

$$Diamido\ diphenyl \atop ketoxine \Big\langle {Naphthionic\ acid. \atop Naphthionic\ acid.}$$

1899. Reddish-brown powder, soluble in water. In concentrated H_2SO_4, blue-violet solution; on dilution, blue ppt.

Application.—A direct cotton colour. Dyes unmordanted *cotton* bluish-red from a soap bath.

COTTON BROWN A (C.). Dark green powder, giving reddish-brown solution in water. In concentrated H_2SO_4, red-violet solution; on dilution, dark brown ppt.

Application.—A direct cotton colour. Dyes unmordanted *cotton* brown from an alkaline salt bath.

COTTON BROWN N (C.). Dark brown powder, soluble in water. In concentrated H_2SO_4, reddish-violet solution; on dilution, reddish-brown ppt.

Application.—As COTTON BROWN A.

COTTON BROWN R (B.) Brown powder. Aqueous and alcoholic solution, yellowish-brown. In concentrated H_2SO_4, bluish-red solution; on dilution, becomes yellowish-brown.

Application.—A direct cotton dye, producing brown shades on unmordanted *cotton*.

COTTON BROWN 3 G and R (Cl. Co.). Similar to Clayton Cotton Brown.

COTTON BROWN R (G.) *v.* POLYCHROMINE B (G.).

COTTON ORANGE G (B.). A tetrazo compound.

$$Primuline - {Metaphenylene\ diamine \atop disulphonic\ acid.}$$

1893. Brown powder, giving yellow solution in water. In concentrated H_2SO_4, brownish-orange solution; on dilution, blue-violet ppt.

Application.—A direct cotton colour, dyeing unmordanted *cotton* orange-yellow from an alkaline salt bath.
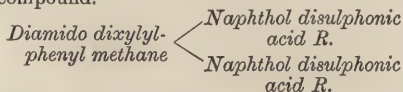
COTTON ORANGE R (B.). A tetrazo compound.

$$Primuline \atop Metanilic\ acid \Big\rangle {Metaphenylene\ diamine \atop disulphonic\ acid.}$$

1893. Brown powder, giving orange-red

solution in water. In concentrated H_2SO_4, bright red solution precipitating on dilution.

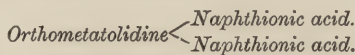*Application.* — As Cotton Orange G, but redder in shade.

COTTON PONCEAU (B. K.). An azo compound.

Diamido dixylyl-
phenyl methane $\left\langle\begin{array}{l}\textit{Naphthol disulphonic} \\ \quad \textit{acid R.} \\ \textit{Naphthol disulphonic} \\ \quad \textit{acid R.}\end{array}\right.$

1887. Red-brown powder, soluble in water. In concentrated H_2SO_4, blue-red solution; unchanged on dilution.

Application. — Used in *lake manufacture*.

COTTON RED (B.). A tetrazo compound.

Orthometatolidine $\left\langle\begin{array}{l}\textit{Naphthionic acid.} \\ \textit{Naphthionic acid.}\end{array}\right.$

1889. Red soluble powder. In concentrated H_2SO_4, blue solution; on dilution, blue ppt.

Application. — A direct cotton colour. Dyes unmordanted *cotton* scarlet-red from an alkaline bath.

COTTON RED 4 B (B.) *v.* Benzopurpurin 4 B.

COTTON SCARLET (B.) *v.* Brilliant Croceïn M (C.).

COTTON SCARLET 3 B concentrated (K.) *v.* Brilliant Croceïn M (G.).

COTTON SPIRITS *v.* Tin Spirits.

COTTON YELLOW G (B.). A tetrazo compound. Combination of *diazotised para-amidoacetanilide* with *salicylic acid*, the hydrolysed product being then combined with $COCl_2$. 1888.

COTTON YELLOW G R, G R R (B.). 1898. Direct cotton dyes, giving bright yellow shades. Soluble yellow powder. In concentrated H_2SO_4, orange-red solution; on dilution, blue-violet ppt.

Application. — A direct cotton dye. Dyes unmordanted *cotton* yellow from an alkaline bath.

COUPIER'S BLUE *v.* Nigrosin Soluble in Spirit.

COW-DUNG. Under this name are usually comprised the various kinds of dung, such as sheep's dung, &c. Animal excrement contains a mixture of phosphates, carbonates, sulphates, chlorides and silicates of calcium, potassium, sodium and ammonium and other salts, albuminoid compounds, fatty acids, fibrous matter, and various other substances. When fresh it never has an acid reaction, but occasionally is slightly alkaline. It is principally employed in fixing the mordants on cotton piece goods prior to these being dyed, so that the white parts shall remain clear. The action of cow-dung has not been completely explained; the phosphates, silicates, and carbonates doubtless exert a fixing action, but the organic substances are not altogether inert. It is known that the latter are cap-able of forming precipitates with metallic oxides — *e. g.*, with *red liquor;* while they also act mechanically by absorbing the loosely adhering mordants and removing them completely from the fibre, so as to prevent them from spoiling the white of the printed goods. It is asserted that cow-dung gives better results than any substitute, such as the arsenates, phosphates, silicates, or carbonates; while it seems to act more slowly and unevenly. The dunging bath is principally formed of cow- or sheep-dung, and should not contain too much straw or iron; before being used it is often allowed to stand for some days with addition of caustic soda, being subsequently diluted with fifty to sixty times its volume of water. The temperature of the dunging bath should be 50° to 65° C.

CRESOTIN YELLOW G (Ber.) (By.). A tetrazo compound.

Benzidine $\left\langle\begin{array}{l}\textit{Orthoöresotic acid.} \\ \textit{Orthocresotic acid.}\end{array}\right.$

1888. Yellow-brown soluble powder. In concentrated H_2SO_4, red-violet solution; becoming on dilution first blue-violet, then greenish-yellow, and finally giving a yellow ppt.

Application. — A direct cotton colour, giving a yellow on unmordanted *cotton* from a soap bath.

CRESOTIN YELLOW R (Ber.) (By.). A tetrazo compound.

Tolidine $\left\langle\begin{array}{l}\textit{Orthocresotic acid.} \\ \textit{Orthocresotic acid.}\end{array}\right.$

1888. Soluble dull brown powder. In concentrated H_2SO_4, violet solution; becoming blue, then green, and finally giving yellow ppt. on dilution.

Application. — *v.* Cresotin Yellow G.

CRESYL BLUE 2 B S (L.). An oxazine colour. Bluish-green powder. Aqueous and alcoholic solution bright blue. Concentrated H_2SO_4, olive-green; on dilution, brown solution.

Application. — A basic dye, producing bright blue shades on *cotton* mordanted with tannin and tartar emetic.

CRESYL BLUE R R N (L.). Similar to the above.

CRESYL FAST VIOLET B B (L.). An oxazine colour. Olive-green powder. Aqueous and alcoholic solution red-violet, with red fluorescence. Concentrated H_2SO_4, brown solution; on dilution, red-violet.

Application. — As Cresyl Blue 2 B S, but gives much redder shades.

CRESYL FAST VIOLET B N (L.). Similar to the above.

CRIMSON SPIRITS *v.* Tin Spirits.

CROCEÏN A Z (C.). Isomeric with Croceïn B.

CROCEÏN B (Sch.).   An azo compound.

Amidoazobenzol — *Naphthol disulphonic acid Sch.*

1884.   Brown-red powder, giving magenta-red solution in water.   In concentrated H_2SO_4, violet solution; on dilution, violet ppt.

Application.—An acid colour.   Dyes *wool* or *silk* in acid bath red.

CROCEÏN 3 B (Sch.).   Similar to above.

Amidoazotoluol — *Naphthol disulphonic acid Sch.*

1884.   Dark brown powder, giving magenta-red solution.   In concentrated H_2SO_4, violet solution; on dilution, violet ppt., then red solution.

Application.—As CROCEÏN B.

CROCEÏN 3 B X (By.) (K.).   An azo colour.

Naphthionic acid — *Beta-naphthol sulphonic acid B.*

1882.   Soluble scarlet powder.   In concentrated H_2SO_4, red-violet solution, becoming red on dilution.

Application.—An acid colour.   Dyes *wool* and *silk* in acid bath red.

CROCEÏN ORANGE (By.) (K.) (Lev.) (B.K.).   *Ponceau 4 G B* (Ber.) (B.K.), *Brilliant orange G* (M.), *Orange G R X* (B.), *Pyrotin orange* (D.), *Orange E N Z* (C.).   An azo compound.

Aniline — *Beta-naphthol sulphonic acid S.*

1878.   Bright red powder, giving orange-red solution in water.   In concentrated H_2SO_4, orange-yellow solution; on dilution, brown ppt.

Application.—An acid colour.   Dyes *wool* and *silk* orange-yellow from an acid bath, which are very fast to light.   Used also in lake making.

CROCEÏN SCARLET 3 B (By.) (K.).   *Ponceau 4 R B* (Ber.).   An azo dye.

Amidoazobenzol sul- — *Beta-naphthol sul-*
phonic acid   *phonic acid B.*

1881.   Brown powder, giving scarlet-red solution in water.   In concentrated H_2SO_4, blue solution; on dilution, yellow-brown ppt., then red solution.

Application.—An acid colour.   Dyes *wool* and *silk* blue-scarlet from an acid bath.   Dyes *cotton* from a concentrated solution acidified with alum.

CROCEÏN SCARLET 4 B (K.) *v.* COCHINEAL RED H (B.).

CROCEÏN SCARLET 7 B (By.).   *Ponceau 6 R B* (Ber.).   An azo compound.

Amidoazotoluol sul- — *Beta-naphthol sul-*
phonic acid   *phonic acid B.*

1881.   Red-brown powder, giving scarlet-red solution in water.   In concentrated H_2SO_4, blue solution, changing to violet-red on dilution.

Application.—An acid colour.   Dyes *wool* and *silk* red from an acid bath.

CROCEÏN SCARLET 10 B (By.).   Brown powder.   Aqueous solution, bluish-red; alcoholic solution, violet.   Concentrated H_2SO_4, greenish blue solution; on dilution, first violet, then bluish-red.

Application.—An acid dye, producing crimson shades on *wool* or *silk*.

CROCEÏN SCARLET 0 extra (K.).   An azo colour.

Amidoazobenzol di- — *Beta-naphthol sul-*
sulphonic acid   *phonic acid B.*

1888.   Soluble scarlet powder.   In concentrated H_2SO_4, blue solution, becoming scarlet on dilution.

Application.—An acid colour.   Dyes *wool* and *silk* scarlet from an acid bath.

CROSS-DYE BLACK (H.).   A sulphide cotton dye, suitable for warp dyeing.

CROSS-DYE DRAB (H.).   A sulphide cotton colour, suitable for warp dyeing; very fast to acids, &c.   (*v.* SULPHIDE COLOURS.)

CRUMPSALL DIRECT FAST BROWN B, O, and **M** (Lev.).   1897.   Direct cotton colours.

CRUMPSALL YELLOW (Lev.).   An azo compound.

Beta-naphthylamine gamma- — *Salicylic*
disulphonic acid   *acid.*

1894.   Yellow powder, soluble in water.   In concentrated H_2SO_4, orange-red solution; unchanged on dilution.

Application.—An acid and a mordant dye.   Dyes *wool* or chrome-mordanted *wool* yellow from an acid bath.

CRYOLITE *v.* ALUMINIUM (ALUMINATE OF SODA).

CRYSTAL CARBONATE *v.* SODIUM CARBONATE.

CRYSTAL PONCEAU (B.) (Ber.).   *Crystal scarlet 6 R* (C.) (M.), *New coccin R* (Ber.).   An azo compound.

Alpha-naphthyl- — *Beta-naphthol gamma-*
amine   *disulphonic acid.*

1885.   Brownish-red glistening crystals, soluble in water.   In concentrated H_2SO_4, violet solution, becoming red on dilution.

Application.—An acid colour.   Dyes *wool* or *silk* red from an acid bath.

CRYSTAL VIOLET (B.) (S.C.I.).   *Crystal violet O* (M.), *Violet C* (P.).   *Hexa-methyl pararosaniline hydrochloride.*   1883.   When anhydrous, forms greenish-brown, glistening crystals; with $8H_2O$, bronzy crystals.   Soluble in water.   In concentrated H_2SO_4, yellow

solution, becoming green, blue, and finally violet on dilution.

Application.—A basic colour. Dyes *wool*, *silk*, or tannin-mordanted *cotton* in neutral bath violet.

CRYSTALLIN, old name for ANILINE.

CUBA WOOD *v.* FUSTIC.

CUDBEAR *v.* ORCHIL.

CUMIDINE PONCEAU *v.* PONCEAU 4 R.

CUMIDINE RED *v.* PONCEAU 4 R.

CURCUMEÏN (Ber.) (B. K.). *Citronin* (D & H.) (F.) (S. C. I.) (O.) (P.), *Jasmin* (G.). An azo colour obtained by action of *nitric acid on diphenylamine orange.* 1880. Ochre-yellow powder, slightly soluble in cold, easily in hot, water. In concentrated H_2SO_4, red-violet solution, becoming olive-brown on dilution.

Application.—An acid colour. Dyes *wool* and *silk* in acid bath orange-yellow.

CURCUMEÏN *v.* FAST YELLOW N (P.).

CURCUMIN *v.* BRILLIANT YELLOW S (B.).

CURCUMIN *v.* TURMERIC.

CURCUMIN S (L.) (Ber.) (By.). *Sun yellow* (G.) (L.) (Ber.) (By.), *Maize.* An azo-oxy compound obtained by boiling *para-nitrotoluene sulphonic acid* with concentrated aqueous $NaOH$. 1883. Red-brown powder, slightly soluble in water. In concentrated H_2SO_4, violet solution, becoming yellow on slight dilution.

Application.—An acid colour. Dyes *wool* and *silk* in acid bath orange.

CUTCH *v.* CATECHU.

CUTICULA *v.* COTTON (PHYSICAL STRUCTURE).

CYANINE *v.* QUINOLINE BLUE.

CYANINE B (M.). An oxidation product of *Patent blue* (M.). 1891. Copper - red powder, giving indigo blue solution in water. In concentrated H_2SO_4, brown-yellow solution, changing to yellow and green on dilution.

Application.—An acid colour. Dyes *wool* and *silk* indigo blue from an acid bath.

CYANOL EXTRA (C.). *Acid blue 6 G* (C.), *Metaoxydiethyl diamido phenylditolyl carbinol disulphonic acid.* 1891. Is closely allied to patent blue. Bluish-black powder, giving a blue solution in water. In concentrated H_2SO_4, yellow solution, becoming green then blue on dilution.

Application.—An acid colour. Dyes *wool* or *silk* bright pure blue from an acid bath.

CYANOL FF (C.). 1899. A similar colour, dyeing purer shades.

CYANOSINE (D. & H.) *v.* PHLOXIN (M.).

CYANOSINE SOLUBLE IN SPIRIT (M.) (K.). A fluoresceïn derivative. *Tetra-bromdichlor fluoresceïn methyl ether.* 1876. Brown-red powder, slightly soluble in boiling water, easily soluble in alcohol. In concentrated H_2SO_4, yellow solution; evolves bromine on heating; on dilution, reddish-brown ppt.

Application.—Dyes *silk* pink from acidified solution.

CYANOSINE B (L.). Sodium salt of *tetrabrom tetrachlor fluoresceïn ethyl ether.* 1882. Red crystalline powder, slightly soluble in water to red-yellow fluorescent solution. In concentrated H_2SO_4, yellowish-brown solution; brownish-red ppt. on dilution.

Application.—*v.* above.

CYCLAMEN (Mo.). Action of *bromine* or *iodine* upon *thionated dichlor fluoresceïne.* 1889. Dark brown powder, soluble in water with non-fluorescent magenta-red colour. In concentrated H_2SO_4, orange-yellow solution; on dilution, brownish-red ppt.

Application.—Dyes *wool* and *silk* bluish-red from a neutral bath.

CURCUPHENINE YELLOW (Cl. Co.). 1897. A direct cotton colour.

D

DAHLIA *v.* METHYL VIOLET B and HOFMANN'S VIOLET.

DARK GREEN (B.). *Solid green O* (M.) (C. R.), *Chlorin* (D. & H.), *Russian green* (L.), *Dinitroso resorcin green, Fast green, Fast myrtle green.* A nitroso compound.

$$C_6H_2(O_2\ 1:3)((NOH)_2\ 2:4).$$
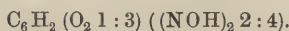
1875. Greyish-brown paste or powder, slightly soluble in cold, easily in hot, water. The dry powder deflagrates on heating. In concentrated H_2SO_4, brown solution; on dilution, brown ppt.

Application.—A mordant dye, producing olive-green shades with iron mordant, brown shades with chrome mordant. Dyes very fast colours.

DELPHIN BLUE (Landoz). Closely allied to *Gallocyanin.* 1894. Olive-brown powder, slightly soluble in water, with a blue-violet colour. In concentrated H_2SO_4, red-violet solution; on dilution, dark blue ppt.

Application,—A mordant dye, giving indigo blue shades with chrome mordant, which are fast to light and milling.

DELTA-PURPURIN 5 B (By.) (Lev.) *v.* DIAMINE RED B (Ber.) (L.).

DELTA-PURPURIN 7 B (By.) (Lev.) (Ber.) (L.) *v.* DIAMINE RED 3 B.

DELTA-PURPURIN G (By.) An azo compound.

Benzidine < Beta-naphthylamine beta-mono-sulphonic acid. Beta-naphthylamine gamma-monosulphonic acid.
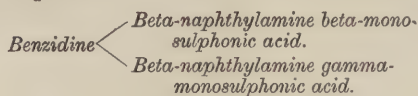
1886. An obsolete, direct cotton dye.

DEXTRIN *v.* THICKENERS ; also COTTON.

DEXTROSE *v.* COTTON (ACTION OF ACIDS).

DIAMINE AZO BLUE R R (C.).
Application.—A direct cotton dye. Dyes unmordanted cotton dark reddish-blue, which on subsequently diazotising and developing with beta-naphthol produces much purer blues, which are very fast to washing.

DIAMINE BLACK B H (C.).   An azo dye.
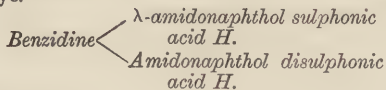
Benzidine $\Big\langle$ *λ-amidonaphthol sulphonic acid H.*
Amidonaphthol disulphonic acid H.

Blue powder.   Aqueous solution, dull blue; alcoholic solution, reddish-blue. Concentrated H_2SO_4, bright blue; on dilution becomes violet.
Application.—A direct dyeing cotton colour. Dyes unmordanted *cotton* greyish-blue from an alkaline salt bath.   May be fixed by treatment with copper sulphate or diazotised and developed with phenylene diamine.

DIAMINE BLACK B O (C.).   An azo dye.
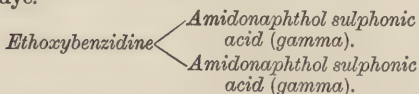
Ethoxybenzidine $\Big\langle$ *Amidonaphthol sulphonic acid (gamma).*
Amidonaphthol sulphonic acid (gamma).

1889.   Black powder, giving blue-black solution in water.   In concentrated H_2SO_4, black-blue solution; on dilution, violet ppt.
Application.—A direct cotton dye.   Dyes unmordanted *cotton* blue to black in an alkaline salt bath.   Shade becomes faster to light by subsequent treatment with copper sulphate.   May also be diazotised and developed (with phenylene diamine) upon the fibre.

DIAMINE BLACK H W (C.).   An azo dye.

Benzidine $\Big\langle$ *λ-amidonaphthol sulphonic acid.*
Paranitraniline $\Big/$ *Amidonaphthol disulphonic acid H.*
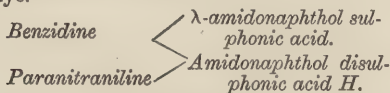
1891.   Greyish-black powder.   Aqueous and alcoholic solution, dull blue.   Concentrated H_2SO_4, bright blue; on dilution, slightly redder.
Application.—A direct cotton black dye, giving greenish-blacks on unmordanted *cotton*. Can be fixed with copper sulphate, but is not suitable for diazotising and developing.

DIAMINE BLACK R O (C.).   An azo dye.

Benzidine $\Big\langle$ *Beta-amidonaphthol sulphonic acid (λ).*
Beta-amidonaphthol sulphonic acid (λ).
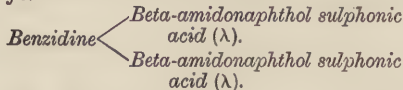
1889.   Black powder, giving a violet-black solution in water.   In concentrated H_2SO_4, blue solution, giving red-blue ppt. on dilution.
Application.—A direct cotton black.   Dyes unmordanted *cotton* fast violet-grey to black.

Shade is rendered still faster by after-treatment with copper sulphate.   Very suitable for diazotising and developing with *naphthylamine ether, beta-naphthol*, &c.

DIAMINE BLACK-BLUE B (C.). *Diamine dark blue B* (C.)   Similar in constitution to *Diamine black H W.*
Application. — A direct cotton colour. Dyes unmordanted *cotton* greyish-blue from an alkaline salt bath.   May be fixed with copper sulphate or bichromate of potash.

DIAMINE BLUE BLACK E (C.).   An azo dye.

Ethoxybenzidine $\Big\langle$ *Amidonaphthol sulphonic acid (λ).*
Beta-naphthol disulphonic acid.
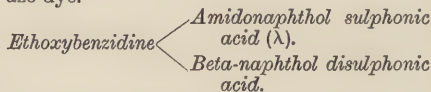
1889.   Black powder, giving blue-black solution in water.   In concentrated H_2SO_4, blue-black solution; on dilution, blue ppt.
Application.—A direct dyeing cotton colour. Gives a blue-black shade on unmordanted *cotton* from an alkaline salt bath.   May be fixed with copper sulphate, or diazotised and developed with *beta-naphthol*, &c.

DIAMINE BLUE 3 B (C.).   *Benzo blue 3 B* (By.), *Congo blue 3 B* (Berlin).   An azo dye.

Tolidine $\Big\langle$ *Amidonaphthol disulphonic acid H.*
Amidonaphthol disulphonic acid H.
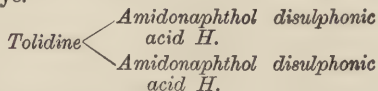
1890.   Grey powder, giving violet solution in water.   In concentrated H_2SO_4, greenish-blue solution; on dilution, violet ppt.
Application. — A direct cotton colour. Dyes unmordanted *cotton* bright blue from an alkaline salt bath.   Cannot be fixed with metallic salts, but gives fast greys when diazotised and developed with *beta-naphthol.*

DIAMINE BLUE 2 B (C.).   *Benzo blue 2 B* (By.), *Congo blue 2 B X* (Berlin).   An azo dye.

Benzidine $\Big\langle$ *Amidonaphthol disulphonic acid H.*
Amidonaphthol disulphonic acid H.
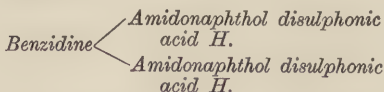
1890.   Grey powder, soluble in water with a violet colour.   In concentrated H_2SO_4, greenish-blue solution; on dilution, violet ppt.
*Application.*—As DIAMINE BLUE 3 B.

DIAMINE BLUE B (C.).   An azo dye.

Ethoxybenzidine $\Big\langle$ *Beta-naphthol sulphonic acid.*
Alpha-naphthol sulphonic acid N W.
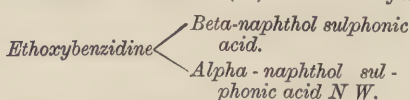
1887.   Now obsolete.

DIAMINE BLUE B X (C.).   *Benzo blue B X* (By.), *Congo blue B X* (Berlin).   An azo dye.

Tolidine < Alpha - naphthol sulphonic acid N W.
Amidonaphthol disulphonic acid H.
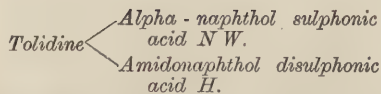
1890. Dark reddish-blue powder, giving a blue violet solution in water. In concentrated H_2SO_4, blue solution; on dilution, violet ppt.

Application.—A greyish-blue direct cotton dye. Dyes unmordanted *cotton* from an alkaline salt bath. Cannot be fixed with metallic salts or diazotised and developed.

DIAMINE BLUE LG, CR, C4R, CB, LR, and DIAMINE CYANINE BLUE (C.) are also sold.

DIAMINE BLUE 3R (C.). An azo dye.

Ethoxybenzidine < Alpha-naphthol sulphonic acid N W.
Alpha-naphthol sulphonic acid N W.

1887. Black powder with greenish reflex. Purple solution in water. In concentrated H_2SO_4, dark blue solution; on dilution, violet ppt.

Application. — A direct cotton colour. Dyes reddish-blue shades from a neutral salt bath. Cannot be fixed with metallic salts or diazotised and developed.

DIAMINE BLUE RW (C.). An azo dye.

Application.—A direct cotton blue. Dyes unmordanted *cotton* indigo blue shades from a neutral salt bath. Cannot be fixed with metallic salts or diazotised and developed. Shades rival vat indigo-blues in fastness.

DIAMINE BORDEAUX B (C.). Reddish-brown powder. Aqueous and alcoholic solution, reddish-blue. Concentrated H_2SO_4, bright blue solution; on dilution, purple solution.

Application.—A direct cotton red. Dyes unmordanted *cotton* claret-red from an alkaline salt bath. Cannot be fixed with metallic salts or diazotised and developed.

DIAMINE BORDEAUX S (C.). Brown powder. Aqueous solution, bluish-red; alcoholic solution, red. Concentrated H_2SO_4, bright blue; on dilution, brown-red ppt., which re-dissolves on further dilution.

Application.—As DIAMINE BORDEAUX B. Used also in *wool* dyeing, giving shades fairly fast to milling.

DIAMINE BRONZE G (C.). An azo colour.

Benzidine < Salicylic acid.
Metaphenylene diamine > Amidonaphthol disulphonic acid H.
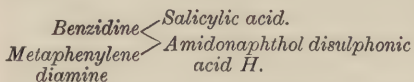
1891. Black powder, insoluble in cold water but soluble on heating, with a chocolate brown colour. In concentrated H_2SO_4, blue-violet solution; on dilution, black ppt.

Application.—A direct cotton colour. Dyes unmordanted *cotton* bronze brown from an alkaline salt bath. May be rendered faster by an after-treatment with chromium fluoride.

DIAMINE BRILLIANT BLUE G (C.). Violet blue powder. Aqueous solution, violet; alcoholic solution, reddish-blue. Concentrated H_2SO_4, greenish-blue solution; on dilution, dull blue, then bluish-red.

Application.—A direct cotton blue. Dyes unmordanted *cotton* indigo-blue from a neutral salt bath. Dyes *wool* with addition of Glauber's salt and acetic acid.

DIAMINE BROWN B (C.). Black powder. Aqueous and alcoholic solution, brown. Concentrated H_2SO_4, violet solution; on dilution, brown ppt.

Application.—A direct cotton colour. Dyes unmordanted *cotton* greyish-brown from an alkaline salt bath. *Wool* is dyed with addition of sodium sulphate and acetic acid. Fastness to washing is much improved by treatment with sulphate of copper after dyeing.

DIAMINE BROWN 3G (C.). An azo dye.

Application. — As DIAMINE BROWN B. Gives yellowish-brown shades.

DIAMINE BROWN M (C.). Bluish-brown powder. Aqueous solution, brownish-red; alcoholic solution, red. Concentrated H_2SO_4, reddish-blue solution; on dilution, becomes brownish-red.

Application. — As DIAMINE BROWN B. Gives reddish-brown shades. May also be diazotised and developed with *beta-naphthol* or *phenylene diamine*, producing in this manner very dark browns.

DIAMINE BROWN V (C.). An azo colour.

Benzidine < Amidonaphthol λ - sulphonic acid.
Metaphenylene diamine.
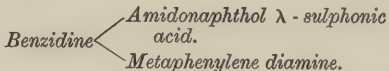
1889. Black powder, insoluble in cold but soluble in hot water, with brownish-red colour. In concentrated H_2SO_4, blue-violet solution; on dilution, brown ppt.

Application.—A direct cotton brown. Dyes unmordanted *cotton* purplish-brown from an alkaline salt bath. May be saddened with copper sulphate or diazotised and developed with *beta-naphthol* or *phenylene diamine*. Dyes *wool* from a slightly acid bath.
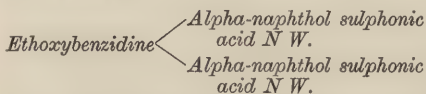
DIAMINE CATECHIN B (C.). Black powder. Aqueous solution, brown; insoluble in alcohol. Concentrated H_2SO_4, violet; on dilution, reddish-blue.

Application.—A direct cotton dye, producing catechu brown shades of unmordanted *cotton*, which are rendered faster by after-treatment with $K_2Cr_2O_7$ or $CuSO_4$.

DIAMINE CATECHIN G (C.). Dark brown powder. Almost insoluble in water, brown solution. Alcoholic solution, brown.

Concentrated H_2SO_4, reddish-blue ; on dilution, brown.

Application.—As above.

DIAMINE CUTCH (C.).   An azo dye.

Naphthylene diamine $<$ *Alpha-naphthol.*
disulphonic acid. *Alpha-naphthol.*

1890.   Greenish - black powder.   Aqueous solution, reddish - blue ; alcoholic solution, dark red.   Concentrated H_2SO_4, reddish-blue solution ; on dilution becomes violet.

Application.—A direct cotton dye, useful only when diazotised and developed.   Dyes *cotton* dull violet from an alkaline salt bath. May be developed with *phenol, fast blue, developer A D,* or *caustic soda solution.*

DIAMINE DEEP BLUE B and R (O.).
Direct cotton blue.

DIAMINE FAST RED F (C.).   An azo dye.

Benzidine $<$ *Beta-amidonaphthol gamma-sulphonic acid.*
Salicylic acid.

1889.   Brownish-red powder, giving a red solution in water.   In concentrated H_2SO_4, violet solution ; on dilution, brown ppt.

Application.—A direct cotton dye, used also for wool.   Dyes *cotton* red from an alkaline salt bath.   May be fixed after dyeing with chromium fluoride.   *Wool* is dyed with addition of sodium sulphate or acetate of ammonia.   If required to be fast to milling is saddened after dyeing, with chromium fluoride or bichromate of potash.   The colour is extremely fast to light.

DIAMINE FAST YELLOW A (C.).
Brownish-orange powder.   Aqueous solution, bright yellow.   Insoluble in alcohol.   Concentrated H_2SO_4, dark red solution ; on dilution, brownish-yellow, then bright yellow.

Application.—A direct cotton colour.   Dyes *cotton* reddish-yellow from a salt bath.   *Wool* is dyed with addition of sodium sulphate and acetic acid.   Colour is very fast to washing (on cotton), milling (on wool), and light.

DIAMINE FAST YELLOW B (C.).
Yellow powder.   Aqueous solution, brownish-yellow ; alcoholic solution, bright yellow. Concentrated H_2SO_4, dark red ; on dilution, light red, then bright yellow.

Application.—v. DIAMINE FAST YELLOW A.

DIAMINE GOLD (C.).   An azo colour.

Diamidonaphthylene $<$ *Phenetol.*
disulphonic acid *Phenetol.*

1890.   Orange-yellow powder, soluble in hot water.   In concentrated H_2SO_4, violet solution ; on dilution becomes first green, then precipitates as brown flocks.

Application.—A direct cotton colour.   Dyes *cotton* gold-yellow from an alkaline salt bath, *wool* from a slightly acid bath.   Fast to washing or slight milling.

DIAMINE GREY G (C.).   An azo dye-stuff of the diamine black group.   Black powder.   Aqueous solution, dark green-blue. Insoluble in alcohol.   Concentrated H_2SO_4, bright blue ; on dilution becomes slightly redder.

Application.—A direct mordant dye.   Dyes unmordanted *cotton* steel-grey from an alkaline bath.

DIAMINE GREEN B (C.).   An azo dye.

Paranitraniline — *Amidonaphthol disulphonic acid H.*
Benzidine $<$ *Salicylic acid.*

1891.   Black powder, giving a dark green solution in water.   In concentrated H_2SO_4, violet solution ; on dilution, blackish ppt.

Application.—A direct cotton colour.   Dyes *cotton* bluish-green from a salt bath.   *Wool* is dyed with addition of sodium sulphate and acetic acid.   Colour is fairly fast to light, washing, and milling.

DIAMINE GREEN G (C.).   Reddish-black powder.   Aqueous solution, greenish.   Easily soluble in alcohol to bluish-green solution. Concentrated H_2SO_4, reddish-blue solution ; on dilution, slightly redder.

Application.—A direct cotton colour.   Dyes unmordanted *cotton* bluish-olive shades.

DIAMINE JET BLACK Cr (C.).   A direct cotton dye, after-treated with bichromate of potash.   Produces deep black shades on unmordanted *cotton* or union material.

DIAMINE JET BLACK OO (C.).   An azo dye.

Application.—A direct cotton colour.   Dyes *cotton* deep black from an alkaline salt bath. Is rendered faster to milling by saddening with bichromate of potash.

DIAMINE JET BLACK R B (C.).   Black powder.   Aqueous solution, bluish-red.   Insoluble in alcohol.   Concentrated H_2SO_4, reddish-blue solution ; on dilution, reddish-blue ppt.

Application.—As DIAMINE JET BLACK OO.

DIAMINE JET BLACK SS (C.).   An azo dye.

Application and Properties.—v. DIAMINE JET BLACK OO.   May also be azotised and developed with *phenylene diamine* or *resorcinol.*

DIAMINE NEW BLUE G (C.).   An azo dye.

Application.—A direct cotton colour.   Dyes *cotton* dull blue from an alkaline salt bath, *wool* from a slightly acid bath.

DIAMINE NEW BLUE R (C.).   An azo dye.   Violet black powder.   Aqueous solution, bright blue ; alcoholic solution, bluish-red.   Concentrated H_2SO_4, reddish blue solution ; on dilution, becomes violet.

Application.—As DIAMINE NEW BLUE G.

DIAMINOGEN B (C.). Reddish-blue powder. Aqueous solution, reddish-blue; alcoholic solution, blue. Concentrated H_2SO_4, bright blue solution; on dilution, becomes violet.

Application.—A direct cotton colour, principally used as a developed colour. Dyes *cotton* greyish-blue from an alkaline salt bath. When diazotised and developed with *phenylene diamine* or *beta-naphthol*, produces a black. *Wool* is dyed with addition of sodium sulphate.

DIAMINOGEN EXTRA (C.). An azo dye.
Application.—As DIAMIDOGEN B.

DIAMINE ORANGE B (C.). An azo dye.
Application.—A direct cotton colour. Dyes *cotton* reddish-orange from an alkaline salt bath. *Wool* is dyed with addition of sodium sulphate and acetic acid.

DIAMINE ORANGE G (C.). Brownish-red powder. Aqueous solution, brown yellow; insoluble in alcohol. Concentrated H_2SO_4, bluish-red; on dilution, becomes bright yellow.

Application.—As DIAMINE ORANGE B, but gives much yellower shades.

DIAMINE PURE BLUE (C.). *Diamine sky blue* (C.), *Benzo sky blue* (By.). An azo dye.

$$Dianisidine \begin{cases} Amidonaphthol\ sulphonic \\ \quad acid\ H. \\ Amidonaphthol\ sulphonic \\ \quad acid\ H. \end{cases}$$

1890. Blue-black powder, soluble in water, with a bright blue colour. In concentrated H_2SO_4, blue-green solution, becoming blue on dilution.

Application.—A direct cotton colour. Dyes *cotton* bright pure blue from a salt bath. *Wool* is dyed with addition of sodium sulphate and acetic acid.

DIAMINE SKY BLUE F F (C.). An azo dye.
Application.—As DIAMINE PURE BLUE, but gives even brighter shades.

DIAMINE RED B (Ber.) (By.) (L.). *Delta-purpurin 5 B* (By.) (Lev.). An azo dye.

$$Tolidine \begin{cases} Beta-naphthylamine\ sulphonic \\ \quad acid\ F. \\ Beta-naphthylamine\ sulphonic \\ \quad acid\ Br. \end{cases}$$

1886. Red-brown powder, soluble in water. In concentrated H_2SO_4, blue solution; on dilution, brown ppt.

Application.—A direct cotton colour. Dyes *cotton* red from an alkaline salt bath.

DIAMINE RED 3 B (Ber.) (By.) (L.). *Delta-purpurin 7 B* (Ber.) (By) (L.). An azo dye.

$$Tolidine \begin{cases} Beta-naphthylamine\ sulphonic \\ \quad acid\ F. \\ Beta-naphthylamine\ sulphonic \\ \quad acid\ F. \end{cases}$$

1886. Red-brown powder, soluble in hot water. In concentrated H_2SO_4, blue solution; on dilution, yellowish-brown solution.
Application.—*v.* DIAMINE RED B.

DIAMINE RED N O (C.). An azo dye.

$$Ethoxybenzidine \begin{cases} Beta-naphthylamine\ sul- \\ \quad phonic\ acid\ Br. \\ Beta-naphthylamine\ sul- \\ \quad phonic\ acid\ F. \end{cases}$$

1887. Greenish crystalline powder, giving a red solution in water. In concentrated H_2SO_4, blue solution; on dilution, black ppt.

Application.—A direct cotton colour. Dyes *cotton* red from an alkaline salt bath. Dyes *wool* from a neutral salt bath.

DIAMINE ROSE B G and G D. 1890. Direct cotton reds.

DIAMINE SCARLET B (C.). An azo dye.

$$Benzidine \begin{cases} Phenetol. \\ Beta-naphthol\ \lambda-disul- \\ \quad phonic\ acid. \end{cases}$$

1889. Reddish crystalline powder, soluble in water. In concentrated H_2SO_4, violet solution, which becomes brown on dilution.

Application.—A direct cotton colour. Dyes *cotton* scarlet-red from a bath containing salt and Turkey-red oil. Dyes *wool* from a slightly acid bath. The colour is very fast to light, washing and acids.

DIAMINE SCARLET 3 B (C.). An azo dye.
Application and Properties.—*v.* DIAMINE SCARLET B.

DIAMINE VIOLET N (C.). An azo dye.

$$Benzidine \begin{cases} Beta-amidonaphthol\ \lambda-sul- \\ \quad phonic\ acid. \\ Beta-amidonaphthol\ \lambda-sul- \\ \quad phonic\ acid. \end{cases}$$

1889. Black-brown powder, giving a red-violet solution in water. In concentrated H_2SO_4, greenish-blue solution; on dilution, reddish-violet precipitate.

Application.—A direct cotton colour. Dyes *cotton* violet from an alkaline salt bath. Dyes *wool* from a neutral salt bath. Fast to light.

DIAMINE YELLOW N (C.). An azo dye.

$$Ethoxybenzidine \begin{cases} Salicylic\ acid. \\ Phenol. \end{cases}$$

1887. Brownish-yellow powder, soluble in water. In concentrated H_2SO_4, violet solution; on dilution, greenish-brown ppt.

Application.—A direct cotton colour. Dyes *cotton* bright yellow from a bath containing soap and sodium phosphate.

DIAMINERAL BLACK B, 3 B, 6 B (C.). Direct cotton dyes, specially suitable for after-treatment with metallic salts.

DIAMINERAL BLUE R (C.). A dye of similar properties to the above.

DIAMOND BLACK (By.).   An azo dye.

Amidosalicylic acid   Alpha-naphthol mono-
azo alpha-naph- —   sulphonic acid
thylamine.   N W.

1889.   Blackish-blue powder, giving a blue-violet solution in water. In concentrated H_2SO_4, green solution; on dilution, violet ppt.

Application.—An acid-mordant dye. Dyes chrome-mordanted *wool* black from an acid bath.   Very fast to light, milling, and acids.

DIAMOND BLACK 2B, F, NG, and NR (By.) are similar colours.

DIAMOND BROWN PASTE (By.). Brown paste, slightly soluble in cold water. Alcoholic solution, brownish-yellow. Concentrated H_2SO_4, brownish-red solution; on dilution, becomes brownish-yellow.

Application.—An acid-mordant dye. Gives brown shades on *wool* mordanted with bichromate of potash.   Used also in *calico printing* with acetate of chrome mordant.

DIAMOND FLAVIN G (By.). An azo dye.

Oxyamidodiphenyl azo salicylic acid.

1891.   Dull yellow-brown paste, insoluble in water. In concentrated H_2SO_4, dark blood-red solution; on dilution, yellowish-brown ppt.

Application. — A mordant dye. Dyes chrome-mordanted *wool* orange-yellow from an acid bath.   Fast to light and milling.

DIAMOND GREEN (By.). An azo dye.

Amidosalicylic acid azo   Dioxynaphthyla-
alpha-naphthylamine.   mine sulphonic acid.

1890.   Black powder, giving violet - black solution in water. In concentrated H_2SO_4, bluish - green solution; on dilution, first greenish - blue solution, then black - violet ppt.

Application.—An acid-mordant dye. Dyes chrome - mordanted *wool* dark bluish - green from an acid bath.

DIAMOND GREEN B (B.) *v.* MALACHITE GREEN.

DIAMOND GREEN G (B.) *v.* BRILLIANT GREEN.

DIAMOND MAGENTA *v.* MAGENTA.

DIAMOND ORANGE (By.)   Similar to DIAMOND YELLOW.

DIAMOND YELLOW G in PASTE (By.). An azo dye.

Meta amidobenzoic acid — Salicylic acid.

1889.   Greyish-yellow paste, slightly soluble in water. In concentrated H_2SO_4, reddish-yellow solution; on dilution, yellow gelatinous ppt.

Application. — A mordant dye. Dyes chrome-mordanted *wool* greenish-yellow.

DIAMOND YELLOW R PASTE (By.). An azo compound.

Orthoamidobenzoic acid — Salicylic acid.

1889.   Brown paste, slightly soluble in water. In concentrated H_2SO_4, reddish-yellow solution; on dilution, brownish-yellow ppt.

Application.—v. DIAMOND YELLOW G.

DIANIL BLACK R and C R (M.).   Direct cotton colours, suitable either for after-treatment with copper salts or diazotising and developing.

DIANIL BLACK H W (M.)   Specially suitable for wool-cotton union material.

DIANIL BLUE B, G & R, 2 R, and 4 R (M.).   *Dianil blue R.*   Reddish-blue powder. Aqueous and alcoholic solution, reddish-blue. Concentrated H_2SO_4, bright blue solution; on dilution, becomes reddish-blue.

Application.—Similar to the above.

DIANISIDINE BLUE (By.) (M.).   The copper salt of an azo dye.

$$Dianisidine \Big\langle \begin{array}{l} Beta\text{-}naphthol. \\ Beta\text{-}naphthol. \end{array} \quad Cu\ salt.$$

1893.   Produced only upon cotton fibre. *v.* AZO COLOURS ON COTTON.

DIANOL BLACK BROWN (Lev.)   Direct cotton brown, which may be fixed by after-treatment with $K_2Cr_2O_7$.

DIANOL BRILLIANT RED (Lev.).   A direct cotton red.

DIANOL BROWN T, Y Y, Y, and R (Lev.).   Direct cotton browns, which may be fixed by after-treatment with $K_2Cr_2O_7$.

DIANOL OLIVE (Lev.).   Direct cotton colour.

DIANTHINE (Br.S.) *v.* SAINT DENIS RED.

DIANTHINE B *v.* ERYTHROSIN.

DIANTHINE G *v.* ERYTHROSIN G.

DIAZINE BLACK (K.).   Black powder. Aqueous solution, dirty green; alcoholic solution, bluish-red.   Concentrated $H_2 SO_4$, olive-green; on dilution, becomes greyish-green.

Application.—A basic dye. Dyes tannin and iron-mordanted *cotton* deep black.

DIAZINE BLUE B (K.).   Brown powder. Aqueous solution, reddish - blue; alcoholic solution, bluish-red.   Concentrated $H_2 SO_4$, brownish-green solution; on dilution, becomes reddish-blue.

Application.—A basic dye. Dyes *cotton* mordanted with tannin and tartar emetic, navy blue.

DIAZINE BROWN (K.).   Greenish - black powder. Aqueous solution, brownish-violet; alcoholic solution, bluish-red.   Concentrated $H_2 SO_4$, dark green solution; on dilution, violet solution, then brownish-red ppt.

Application.—A basic dye. Dyes tannin-mordanted *cotton* dark brown.

DIAZINE GREEN (K.).   Bluish - brown powder.   Aqueous and alcoholic solution, bright blue.   Concentrated $H_2 SO_4$, olive-green solution; on dilution, greenish-blue, then reddish-blue.

Application. — Dyes tannin - mordanted *cotton* dark olive - green.

DIAZO BLACK B (By.). An azo dye.

Benzidine ⟨ *Alpha-naphthylamine sulphonic acid L.* / *Alpha-naphthylamine sulphonic acid L.*

Greyish - black powder. Aqueous solution, reddish-blue; alcoholic solution, blue. Concentrated H_2SO_4, bright blue solution; on dilution, becomes reddish-blue.

Application. — A direct cotton colour, which requires diazotising and developing. Dyes *cotton* dull grey shades, which become much darker by diazotising and developing with beta-naphthol.

DIAZO BLACK 3 B, G, H, B H N, and R. Similar colours to the above.

DIAZO BLUE 3 R (By.). Black powder. Aqueous solution, reddish - blue; alcoholic solution, bluish-red. Concentrated H_2SO_4, reddish-blue solution; unchanged on dilution.

Application. — v. DIAZO BLACK B.

DIAZO BLUE (B.). Similar to the above.

DIAZO BLUE BLACK (By.). Greyish-black powder. Aqueous solution, bright blue. Insoluble in alcohol. Concentrated H_2SO_4, light blue solution; unchanged on dilution.

Application. — v. DIAZO BLACK B.

DIAZO BRILLIANT BLACK B (By.). An azo dye.

Tolidine ⟨ *Alpha-naphthylamine sulphonic acid L.* / *Alpha-naphthylamine sulphonic acid L.*

Greenish-black powder. Aqueous solution, bright blue; alcoholic solution, bright red. Concentrated H_2SO_4, reddish-blue; on dilution, blue ppt., which dissolves on further dilution to a bright blue solution.

Application. — v. DIAZO BLACK B.

DIAZO BRILLIANT BLACK R (By.). Similar colour to the above.

DIAZO BORDEAUX (By.). Closely allied to *Primuline.* Yellow powder. Aqueous solution, yellow; alcoholic solution, yellow with green fluorescence. Concentrated H_2SO_4, brown solution; on dilution, yellow ppt., which re-dissolves on further dilution.

Application. — v. PRIMULINE.

DIAZO BROWN G (By.). Black powder. Aqueous solution, reddish - blue; alcoholic solution, brown. Concentrated H_2SO_4, dark bluish-green solution; on dilution, bluish-red, then brown ppt., then brown solution.

Application. — v. DIAZO BLACK B.

DIAZO BROWN R EXTRA (By.). Similar colour to the above.

DIAZO FAST BLACK (M.). A direct cotton colour developed on the fibre.

DIAZO FAST BLACK H (By.). Similar to the above.

DIAZURIN B (By.). An azo dye.

Dianisidine ⟨ *Alpha-naphthylamine sulphonic acid L.* / *Alpha-naphthylamine sulphonic acid L.*

Greenish-black powder. Aqueous and alcoholic solution, bluish - red. Concentrated H_2SO_4, bright blue solution; unchanged on dilution.

Application. — A direct cotton dye, which requires developing. Dyes *cotton* dull violet, which is converted into navy blue by developing with beta-naphthol.

DIAZURIN G (By.). A similar colour to the above.

DIGALLIC ACID v. TANNIC ACID.

DIMETHYLANILINE ORANGE v. ORANGE III.

DIOXINE (L.). *Gambine B* (H.). A nitroso compound.

Nitroso dioxynaphthalene.

1889. Red paste, insoluble in water. In concentrated H_2SO_4, green solution; on dilution, red ppt.

Application. — A mordant dye. Dyes chrome - mordanted *wool* brown and iron-mordanted wool green. Fast to light and milling.

DIPHENYLAMINE BLUE v. BAVARIAN BLUE D B F.

DIPHENYLAMINE ORANGE v. ORANGE IV.

DIPHENYLANILINE BLUE SOLUBLE IN SPIRIT (D. & H.). *Bavarian Blue Spirit Soluble* (Ber.). A triphenyl carbinol derivative.

Triphenyl pararosaniline hydrochloride.

1866. Brown powder. Insoluble in water; soluble in alcohol. In concentrated H_2SO_4, brown solution; on dilution, blue ppt.

Application. — Principally employed for preparing *alkali* and *soluble blues.* Used a little in *silk* dyeing, giving a bright blue in a slightly acid bath.

DIPHENYL BLUE 2 G, B, and 2 R (G.). 1899. Direct cotton blues.

DIPHENYL ORANGE G G and R R (G.). 1899. Direct cotton yellows.

DIRECT BLUE (M.). A direct cotton dye.
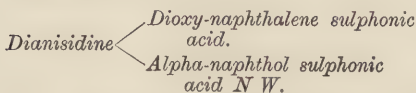
DIRECT or ONE - DIP BLACKS v. BLACKS, DIRECT OR ONE-DIP.

DIRECT BLUE B (K.). Blue powder. Aqueous and alcoholic solution, reddish-blue. Concentrated H_2SO_4, bright blue solution; on dilution, becomes violet.
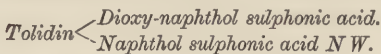
Application. — A direct cotton colour. Dyes unmordanted *cotton* bright reddish-blue.

DIRECT BLUE 2BX and 3BX (K.). Similar to the above, but give purer shades.

DIRECT BLUE B (S.C.I.). An azo dye.

$$Dianisidine \begin{cases} Dioxy\text{-}naphthalene\ sulphonic \\ \quad acid. \\ Alpha\text{-}naphthol\ sulphonic \\ \quad acid\ N\ W. \end{cases}$$

1891. Dark green powder, with metallic lustre. Soluble in water, with a reddish-blue colour. In concentrated H_2SO_4, greenish-blue solution; on dilution, violet ppt.

Application.—A direct cotton dye. Dyes *cotton* blue from an alkaline salt bath.

DIRECT BLUE R (S.C.I.). An azo dye.

$$Tolidin \begin{cases} Dioxy\text{-}naphthol\ sulphonic\ acid. \\ Naphthol\ sulphonic\ acid\ N\ W. \end{cases}$$

1891. Blue-black powder, giving a violet solution in water. In concentrated H_2SO_4, blue solution; on dilution, violet ppt.

Application.—A direct cotton colour. Dyes *cotton* dark violet from an alkaline salt bath.

DIRECT BLUE-BLACK B (By.). Black powder. Aqueous solution, dull reddish-blue; alcoholic solution, similar. Concentrated H_2SO_4, dull blue; on dilution, becomes reddish blue.

Application.—A direct cotton dye. Gives blue-black shades on unmordanted *cotton*.

DIRECT BROWN J (S.C.I.). An azo dye.

$$\begin{matrix} Meta\text{-}amidobenzoic\ acid \\ \\ Meta\text{-}phenylene\ diamine \\ \\ Meta\text{-}amidobenzoic\ acid \end{matrix} \begin{cases} Meta\text{-}phenylene \\ \quad diamine \\ Meta\text{-}phenylene \\ \quad diamine \end{cases}$$
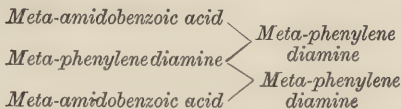
1891. Brown powder, giving a yellow-brown solution in water. In concentrated H_2SO_4, brown solution; on dilution, brown ppt.

Application.—A direct cotton colour. Dyes *cotton* brown from an alkaline salt bath. May be fixed with metallic salts or diazotised and developed with resorcinol.

DIRECT BROWN R (G.). This is obtained by dyeing with *Polychromine B* (*q.v.*) and developing with *Meta-phenylene diamine*.

DIRECT COTTON COLOURS. A great number of dyestuffs are now in use which are distinguished by the common property of dyeing the vegetable fibres in full shades, fairly fast to washing, without the aid of mordants. The first of these substances was Congo red, which was discovered in 1884 by Bœttiger, hence the whole group, especially the derivatives of *benzidine* and *tolidine*, which are chemically related to this dyestuff, are frequently called the *Congo colours* or *Benzidine colours*. The direct cotton colours which are articles of commerce at the present time are, mainly, sulphonates of sodium,

ammonium, or potassium. Most of them are tetrazo compounds—*i.e.*, compounds which contain the azo group $-N=N-$ twice in the molecule.

Like the ordinary azo colours, the tetrazo colours are produced by the action of diazotised amines on phenols (naphthols) or aromatic amines on their sulphonic or carboxylic acids; thus they contain, in addition to the double chromophorous group N_2, the auxochromous groups "NH_2" or "OH"; or such derivatives, as "$NH(C_6H_5)$" or "OC_2H_5."

The tetrazo colours are derivatives of *benzidine* or *tolidine* (Congo colours), *amidostilbene*, *azoxy diamines*, and various other diamines. In addition to the tetrazo colours, a class of direct cotton colours is known, which are either not azo compounds at all, or the tinctorial character of which is not due, in the first place, to the azo group. The dyestuffs of this group are obtained from compounds, which are prepared by heating organic bases, notably *paratoluidine* and *metaxylidine*, with sulphur. In this way "thio-bases" are obtained, the chromophorous group of which has the constitution $\begin{smallmatrix} S \\ N \end{smallmatrix}\!\!> C-$. The first of these compounds was *primuline*, discovered by A. G. Green. Neither *primuline* nor a similar colouring matter, named *thioflavin S*, are azo compounds. Several other dyestuffs—*e.g.*, *Erika*, *cotton yellow R*, and in a certain sense, also *thiazol yellow*—are azo compounds; but undoubtedly they possess the same chromophorous group as primuline, so that the azo group need not be considered as an essential condition for the colouring character of these compounds.

The direct cotton colours possess the property of forming lakes with the basic colours. E. Knecht [*] and G. Galland [†] have studied this reaction, which was first made known in the case of *chrysamin* by the Bayer Co. They found that only the basic colours form lakes with those dyestuffs, and that the lakes are decomposed above 70° and even at lower temperatures.

Use is made of the property to produce compound shades by first dyeing with a direct colour and subsequently topping with a basic colour.

DIRECT GREY B (M.). Dark violet powder. Aqueous solution, bright blue; alcoholic solution, reddish-blue. Concentrated H_2SO_4, dull blue solution; on dilution, reddish-blue.

Application.—A direct cotton dye.

DIRECT GREY G (M.). Is a similar product.

---

[*] *Journ. Soc. Dyers and Col.*, 1886, p. 2.
[†] *Ibid.*, 1886, p. 145.

DIRECT COTTON DYES (for Names of Makers, &c., see Alphabetical Description of Dyes).

Reds.

Atlas Red.
Azo Corinth.
  ,, Mauve B, R.
  ,, Orseillin.
  ,, Purpurin 4 B.
Benzidine Red.
Benzo Fast Red.
  ,, Purpurins.
Brahma Red.
Brilliant Congo G, R.
  ,,   Geranine B, 3 B.
  ,,   Purpurin 5 B, R.
Chloramine Red 4 B, 8 B.
Chicago Red.
Cloth Red.
Columbia Red 8 B.
Congo Corinth B, G.
  ,, Reds.
  ,, Rubin.
Cotton Bordeaux.
  ,, Reds.
Delta-purpurin 5 B, 7 B.
Diamine Bordeaux B, S.
  ,,   Fast Red F.
  ,,   Red 10 B, 5 B, 3 B.
        B, N O.
  ,,   Rose, B G, G D.
  ,,   Scarlet 3 B, B.
Dianol Brilliant Red.
Dianthine.
Direct Cotton Red.
  ,, Red.
  ,, Scarlet B, G S, R.
Erika B G, B N, 2 G N, 4 G N.
Geranine B, 2 G.
Gladiolin.
Glycin Red.
Hessian Bordeaux.
Naphthylene Red.
New Direct Red.
New Red.
Oxamine Maroon.
  ,,   Red B.
  ,,   Scarlet.
Roseazurin B, G.
Rosophenin Geranine.
  ,,   Pink 10 B.
Salmon Red.
St. Denis Red.
Stilbene Red.
Terra-cotta F.
Thiazine Red R G.
Titan Pink.
  ,, Red.
  ,, Scarlet, C, S.
Toluylene Red.

Oranges and Yellows.

Azo Orange.
Benzo Orange R.

Brahma Orange.
Brilliant Orange G.
  ,, Yellow.
Chicago Orange G, 2 R, 3 R.
Chloramine Orange.
  ,,   Yellow.
Chlorophenin.
Chromine G.
Chrysamine, G, R.
Chrysophenine G, G S.
Clayton Yellow.
Cloth Orange.
Columbia Orange.
  ,, Yellow.
Congo Orange G, R.
Cotton Orange.
  ,, Yellow.
Cresotine Yellow.
Curcumin S, S extra, W.
Curcuphenine.
Diamine Fast Yellow A B.
  ,,   Gold.
  ,,   Orange B, G.
  ,,   Yellow N.
Diazo Bordeaux.
  ,,   Chromine B G.
Diphenyl Citronine G.
  ,,   Orange G G, R R.
Direct Orange 2 R, T.
  ,,   Yellow A S C, G, 2 G,
        R, S, T.
Fast Diphenyl Yellow.
Hessian Yellow.
Mekong Yellow.
Mikado Gold Yellow, 2 G, 4 G,
        6 G, 8 G.
  ,,   Orange G O, R O,
        2 R O, 3 R O, 4 R O.
  ,,   Yellow.
Mimosa Yellow.
Nitrophenin.
Orange T A.
Oriol.
Oxamine Orange G.
Oxyphenin.
Polyphenyl Yellow.
Primuline.
Pyramine Orange, 3 G.
Stilbene Orange 4 R.
  ,,   Yellow 6 G, G.
Sulphanil Yellow.
Thianil Yellow.
Thiazol.
Thioflavin S.
Titan Yellow G, R.
Toluylene Orange G, R, 2 R.
Turmerine.

Greens.

Benzo Dark Green, B, G G.
  ,, Green, 2 B, G.

Benzo Olive.
Brilliant Benzo Green B.
Columbia Green.
Diamine Green B, G.
Dianol Olive.
Direct Green T.
Eboli Green.
Oxamine Green M.

Blues.

Azo Blue.
Azo Navy Blue.
Benzidine Blue.
Benzoazurine G, 3 G, 5 G, R.
Benzo Black Blue G, 5 G, R.
  ,,   Blue 2 B, 3 B, B X, 2 R,
        4 R, R A.
  ,,   Chrome Black Blue B.
  ,,   Cyanine 3 B, B, R.
  ,,   Indigo Blue.
  ,,   Mauve Blue.
  ,,   Red Blue G, R.
  ,,   Sky Blue 4 B.
Blue I C R.
  ,, for half wool.
Brilliant Azurin B, 5 G.
  ,,   Benzo Blue 6 B.
  ,,   Sulphonazurin B.
Chicago Blue 6 B, 4 B, B, R,
        2 R, 4 R, R W.
Chlorazol Blue.
Columbia Blue G, R.
  ,,   Fast Blue 2 G.
Congo Blue 2 B.
  ,,   Fast Blue B, R.
Diamine Azo Blue R.
  ,,   Blue 3 B, 2 B, B X,
        B G, B, 6 G, 3 R.
  ,,   Brilliant Blue G.
  ,,   Dark Blue B.
  ,,   Deep Blue B, R.
  .,   New Blue G, R.
  ,,   Sky Blue.
Diamineral Blue R.
Diamogene Blue 2 B, B, G
    extra.
Dianil Blue B, G, R, 2 R, 4 R.
Dianthine Blue.
Diazo Blue 3 R.
  ,,   Indigo Blue B.
  ,,   Navy Blue, 3 B.
  ,,   Red Blue 3 R.
Diazurine B, G.
Diphenyl Blue 2 G, B, 2 R.
Direct Blue B, 3 B X, R.
Eboli Blue B.
Erie Blue, 2 G.
Glycin Blue.
Heligoland Blue 3 B.
Indazurine 5 G M.
Metazurine B.

Naphthamine **Blue 2** B, 3 B,
  5 B, R, 3 R.
Naphthazurine 2 B, R
Naphthyl Blue 2 B.
New Toluylene Blue.
Oxamine Blue 2 B.
Pacific Blue B, 4 B.
Paramine Blue.
   ,,   Indigo Blue.
   ,,   Navy Blue R, 2 R.
Sulphonazurin D.
Sulphoncyanin G, G R, 3 R.
Titan Blue.
   ,,   Como.
   ,,   Navy R.
Toledo Blue V.
Toluidine Blue.
Toluylene Blue.
   ,,   Dark Blue.
Trisulphon Blue B, R.
Zambesi Blue B X, R X.

Purples and Violets.

Azo Corinth.
  ,, Mauve B, R.
  ,, Violet.
Congo Corinth B, G.
   ,,   Violet.
Diamine Violet **N**.
Diazo Violet R.
Glycin Corinth.
Heliotrope 2 B.
Hessian Brilliant Purple.
   ,,   Purple B, D, N B,
        N G.
   ,,   Violet.
Oxamine Violet G R, R R,
  B B R.
Oxydiamine Violet.
Trisulphon Violet B.

Browns.

Benzo Black Brown.
   ,,   Brown B, B R, 5 R, G,
       M B X.
   ,,   Chrome Brown B, B S,
       G, 5 G, R, 3 R.
   ,,   Dark Brown.
   ,,   Nitrol Brown, G, 2 R.

Catechu Brown 3 D X, 2 D X,
  D, 2 D, 3 D, F D K, F K,
  G K, 2 G K.
Chicago Brown B, G.
Chloramine Brown G.
Clayton Cotton Brown.
Cloth Brown (red shade).
   ,,   (yellow shade).
Columbia Brown R.
Congo Brown B, R, V B B.
Cotton Brown A, N, R.
Crumpsall Direct Fast Brown
  B, O, M.
Diamine Bronze G.
   ,,   Brown B, M, V, 3 G.
   ,,   Catechine B, G.
   ,,   Cutch.
   ,,   Nitrazol Brown B,
       G, B D, R D.
Dianol Black Brown.
   ,,   Brown Y Y, Y, R, T.
Diazo Brown G, R extra., V.
Diphenyl Brown B N, G N,
  R N, R G.
Direct Bronze Brown.
   ,,   Brown R, Y.
   ,,   Cotton Brown G, R.
   ,,   Fast Brown B, 2 G.
Durophenin Brown V.
Hessian Brown 2 B M, 2 M.
Mikado Brown 2 B, B, G,
  3 G O, M.
New Toluylene Brown B,
  B B O, M, R,
Paramine Brown C, R.
Pega Brown G.
Pluto Brown R, N B, G G.
Sulphon Brown R.
   ,,   Dark Brown.
Thiazine Brown G, R.
Titan Brown Y.
Toluylene Brown B B O, B,
  G, M, R, V O.
Trisulphon Brown G, G G.
Zambesi Brown G, 2 G.

Blacks.

Benzo Black, S extra.
   ,,   Chrome Black B G N.

Benzo Fast Black.
   ,,   Fast Grey.
   ,,   Nitrol Black, B, **T**.
Carbide Black B, R.
Chromanil B F, 2 B F, 3 B F,
  R F, 2 R F.
Columbia Black B, 2 B, 2 F
  extra, R.
   ,,   Chrome Black.
Diamine Black B O, B H,
      HW, R O, R O O.
   ,,   Blue Black E.
   ,,   Grey G.
   ,,   Jet Black O O, S S,
       Cr, R B.
   ,,   Nitrazol Black.
Diamineral Black B, 3 B,
  6 B.
   ,,   Black Blue R.
Diazo Black 3 B, B, H, R,
  R extra.
   ,,   Blue Black.
   ,,   Brilliant Black B, R.
   ,,   Fast Black.
Dianil Black G, R.
Diphenyl Blue Black.
Direct Blue Black B, **N**.
   ,,   Deep Black E.
   ,,   Jet Black G, T,
       R W.
   ,,   Grey B R.
   ,,   Triamine Black B X,
       G X.
Grounding Black.
Isodiphenyl Black R.
Nyanza Black B.
Oxamine Black B R.
Oxydiamine Black A, N,
  S O O O.
Paramine Blue Black S.
Pluto Blacks.
Polyphenyl Black B.
Sulphon Black 3 B, 4 B T.
Tabora Black.
Titan Grey.
Triamine Black B, B T.
Union Black B, 2 B, S.
Violet Black.
Zambesi Black B, B R, D F,
  R.

DIRECT GREY B (S.C.I.). An azo colour.

$Tolidine\!\!<\genfrac{}{}{0pt}{}{Dioxynaphthoic\ sulphonic\ acid.}{Dioxynaphthoic\ sulphonic\ acid.}$

1891. Dark grey powder, soluble in hot water with a blue-violet colour. In concentrated H_2SO_4, bluish solution ; on dilution, blue grey ppt.

Application.—A direct cotton colour. Dyes *cotton* grey from a salt bath.

DIRECT GREY R (S.C.I.). A similar colour to the above.

$Tolidine\!\!<\genfrac{}{}{0pt}{}{Dioxynaphthoic\ sulphonic\ acid.}{Naphthol\ sulphonic\ acid\ N\,W.}$

1891. Blue-black powder, soluble in water with a violet colour. In concentrated H_2SO_4, blue solution ; on dilution, violet ppt.

Application—v. DIRECT GREY B.

DIRECT JET BLACK R and T (By.). Direct *cotton* colours.

DIRECT ORANGE (Fi.). A direct *cotton* dye.

DIRECT ORANGE 2 R (K.). An azo compound obtained by reduction of DIRECT YELLOW (K.). 1892. Brown powder, giving orange-red solution in water. In concentrated H_2SO_4, bright blue solution, which becomes orange on dilution.

Application.—A direct cotton colour. Dyes *cotton* orange from a salt bath; suitable for leather.

DIRECT RED (Ber.) (By.). An azo dye.

$$Diamidophenyltolyl \bigg\langle \begin{array}{l} Naphthionic\ acid. \\ Naphthionic\ acid. \end{array}$$

1888. Red powder, soluble in water. In concentrated H_2SO_4, blue solution; on dilution, dark blue ppt.

Application.—A direct cotton colour. Dyes *cotton* red from an alkaline salt bath.

• **DIRECT RED** (Fi.). Dark red powder. Aqueous solution, bright red; alcoholic solution, pink. Concentrated H_2SO_4, bluish-red; on dilution, becomes bright red.

Application.—A direct *cotton* colour.

DIRECT SCARLET R (K.). Reddish-brown powder. Aqueous and alcoholic solution, bright red. Concentrated H_2SO_4, bluish-red solution; unchanged on dilution.

Application.—A direct cotton dye.

DIRECT YELLOW (Ber.) (By.). An azo dye.

$$Diamidophenyltolyl \bigg\langle \begin{array}{l} Salicylic\ acid. \\ Salicylic\ acid. \end{array}$$

1888. Dark greyish-brown powder, giving a yellow solution in water. In concentrated H_2SO_4, carmine-red solution; on dilution, yellow-brown ppt.

Application.—A direct cotton colour. Dyes *cotton* yellow from an alkaline salt bath.

DIRECT YELLOW (Fi.). A direct cotton dye.

DIRECT YELLOW G (K.). A nitro-stilbene compound. Produced by the action of caustic soda on *paranitrotoluol sulphonic acid.* 1892. Red-brown powder, giving reddish-yellow solution in water. In concentrated H_2SO_4, cherry-red solution, becoming yellow on dilution.

Application.—A direct cotton colour. Dyes *cotton* yellow from a salt bath.

DIRECT YELLOW 2 G, 3 G (K.). *v.* MIKADO GOLD YELLOW.

DIVI-DIVI. This, like myrabolams and bablah, is a dried fruit. It is produced by *Cæsalpinia coriaria*, and is grown chiefly in West Indies and in South America. It forms flattened pods, 3 to 4 inches long, $\frac{1}{2}$ to $\frac{3}{4}$ inch wide, and very thin. The pods are hard and brittle, brown or black externally, and buff or yellow in the interior. They contain 20 to 35 per cent. tannin (ellagitannic acid) and much brown colouring matter. They are employed to some extent in black dyeing.

DOLOMITE *v.* CALCIUM CARBONATE.

DOUBLE ANTIMONY FLUORIDE *v.* ANTIMONY (SODIUM FLUORIDE).

DOUBLE BRILLIANT SCARLET G (Ber.) (Lev.). *Scarlet for silk* (M.). An azo compound.

$$Beta\text{-}naphthylamine\ sulphonic\ acid\ Br. - Beta\text{-}naphthol.$$

1882. Reddish-brown powder, giving yellowish-red solution in water. In concentrated H_2SO_4, magenta-red solution; on dilution, brownish-red ppt.

Application.—An acid colour. Dyes *wool* and *silk* yellowish-red from an acid bath.

DOUBLE BRILLIANT SCARLET 3 R (By.) *v.* DOUBLE SCARLET EXTRA S.

DOUBLE GREEN S F (K.) *v.* METHYL GREEN.

DOUBLE MURIATE OF TIN *v.* TIN (STANNOUS CHLORIDE).

DOUBLE SCARLET EXTRA S (Ber.) (Lev.). *Double brilliant scarlet 3 R* (By.), *Brilliant ponceau 4 R* (By.). An azo dye.

$$Beta\text{-}naphthylamine\ sulphonic\ acid\ Br - Alpha\text{-}naphthol\ sulphonic\ acid\ N\ W.$$

1882. Brownish-red powder, giving a yellowish red solution in water. In concentrated H_2SO_4, magenta-red solution, becoming yellow-red on dilution.

Application.—An acid dye. Dyes *wool* and *silk* scarlet-red from an acid bath.

DOUBLE SCARLET R (Lev.). *v.* AZO COCCIN 2 R.

DRAGON GREEN. Old name for MALACHITE GREEN.

DUNG SALT *v.* SODIUM ARSENATE.

DUROPHENINE (Cl. Co.). Direct cotton brown, fixed with metallic salts.

DYER'S BROOM (*Genista tinctoria*) is used in dyeing yellow upon leather.

DYER'S WOODRUFF (*Asperula tinctoria*). A common English garden plant. May be employed as a substitute for madder, its roots containing a small amount of alizarin.

DYES, ACTION OF LIGHT UPON. The fading of colours under the action of light has been a frequent subject of investigation, but the most systematic series of experiments of which the results have been published on the point are those of J. J. Hummel.[*] In these experiments the various natural and artificial dyes are classified into groups according to their relative resistance to the action of light.

Each dyed pattern was divided into six pieces, one of which was protected from the action of light, while the others were exposed behind glass for different periods of time in weather-proof, but not air-tight, cases erected in an open position with a south aspect.

[*] *Brit. Assoc. Reports*, Section B., 1893, 1894, 1895, 1896, and 1893.

The shortest period of exposure, or "fading period," was about three weeks (May 24 to June 14, 1892), and a record of the fading power of this period was kept by exposing along with the patterns a special series of "standards" dyed with selected colouring matters. The standards were removed from the action of the light along with the first set of dyed patterns at the end of the first "fading period" (May 24 to June 14, 1892). The faded standards were then at once replaced by a fresh unexposed series, and these were allowed to fade to the same extent as the first, when, a second period of exposure equal in fading power to the first having thus been marked off, a second set of the dyed patterns were removed from the action of light along with the second series of faded standards. The latter were again renewed as before to mark off the next "fading period." The fourth and fifth sets of dyed patterns were submitted to an exposure equivalent to two or three "fading periods" in order that the fifth set might have an exposure of about one year.

The above method was adopted in order to be able to expose dyed patterns to an equal amount of fading in different years, irrespective of the time of the year or the conditions of light, moisture, temperature, &c. It was rendered necessary in consequence of the practical impossibility of exposing simultaneously a complete set of dyed colours.

The following groups were distinguished :—

    Class I.—Very Fugitive Colours.
      ,,   II.—Fugitive Colours.

    Class III.—Moderately Fast Colours.
      ,,   IV.—Fast Colours.

    Class V.—Very Fast Colours.

RED DYES.

Class I.—Very Fugitive Colours.

TRIPHENYLMETHANE COLOURS.

Phthaleins—
    Bengaline P H.
    Bengale Red B.
    Cyanosin.
      ,,   B.
    Cyclamine.
    Eosin A.
      ,,   S.
      ,,   F.
      ,,   B N.
    Erythrosin G.
      ,,   J N.
    Methyl-eosin.
    Phloxin.
      ,,   P.
      ,,   T extra.
    Rose Bengale N T.
      ,,   ,,   N T O.

AZINE COLOURS.

Diamidophenazin Nitrate.
Fuchsia.
Neutral Red.
Safranine.

INDULINE COLOURS.

Rosinduline 2 G.
      ,,   G.

AZO COLOURS.

Naphthylene Red.
Primuline Red.
Rosazurin B.
      ,,   G.
Roxamine.
Terra Cotta F.

NATURAL COLOURING MATTERS.

Barwood (Al mordant).
Sanderswood (Al mordant).
Orchil.

Class II.—Fugitive Colours.

TRIPHENYLMETHANE COLOURS.

Rosanilines—
    Acid Magenta.
    Acetic Acid Rubin.
    Magenta.
    New Magenta.
    Pararosaniline.
    Rosanilin.

Phthaleins—
    Rhodamine.
      ,,   B extra.
      ,,   G.
      ,,   G extra.

DIPHENYLMETHANE COLOURS.

Acridine Red.
Pyronine G.

AZINE COLOURS.

Magdala Red.

AZO COLOURS.

Acid Colours—
    Acid Ponceau.
    Azo Orchil R.
      ,,   Cardinal G.
    Bordeaux.
    Cloth Red 3 B extra.
      ,,   3 G   ,,
    Caroubier.

Clayton Cloth Red.
Cresol Red.
Double Brilliant Scarlet G.
Emin Red.
Fast Acid Magenta.
Fast Red A.
,,　　B.
,,　　B T.
Milling Red G.
,,　　R.
Naphthol Rubin.
Orchil Substitute N.
,,　　　,,　　V.
,,　　　,,　　3 V N.
Phenanthrene Red.
Ponceau 2 S.
Thiorubin.

Direct Cotton Colours—
Benzo Purpurine B.
,,　　　,,　　4 B.
,,　　　,,　　6 B.
,,　　　,,　　10 B.
,,　　Fast Red.
Brilliant Geranine B.
,,　　　,,　　3 B.
Congo 4 R.
,,　　G R.
,,　　Red.
,,　　Rubin.
Delta-purpurine 5 B.
,,　　　,,　　7 B.
,,　　　,,　　G.
Diamine Red N O.
Direct Red.
Hessian Brilliant Purple.
,,　　Purple B.
,,　　　,,　　D.
,,　　　,,　　N.
Titan Red.
,,　　Scarlet C.

NATURAL COLOURING MATTERS.

Barwood (Sn mordant).
Camwood (Al and Sn).
Limawood (Al and Sn).
Sanderswood (Sn).
Ventilago Madraspatana (Al and Sn mordant).

Class III.—Moderately Fast Colours.

INDULINES.

Rosinduline B.
,,　　2 B.

AZO COLOURS.

Acid Colours—
Azo Bordeaux.
,,　　Carmine B X.
,,　　Cochineal.
,,　　Eosin.

Azo Red A.
Anisol Red.
Anthracene Red.
Brilliant Scarlet G G.
,,　　　,,　　G.
Buffalo Rubin.
Coccin 2 B.
Coccinin.
Cochineal Scarlet 2 R.
,,　　　,,　　4 R.
,,　　　,,　　R.
Crocein Scarlet O F X.
,,　　　,,　　10 B.
,,　　Red G extra.
,,　　　,,　　O G.
,,　　B.
Crystal Ponceau.
Double Brilliant Scarlet 2 R.
Fast Red G.
,,　　E.
,,　　D.
Fast Wool Red.
Granat.
Lake Scarlet G G.
,,　　　,,　　R.
Milling Scarlet.
Naphthol Scarlet.
Œanthin.
Orchil Substitute.
Palatine Red.
Persian Red.
Ponceau R.
,,　　2 R.
,,　　3 R.
,,　　4 R.
,,　　10 R B.
Pyrotin Red.
Scarlet G.
,,　　B.
,,　　G R.
,,　　2 R.

Direct Cotton Colours—
Brilliant Congo R.
,,　　　,,　　G.
,,　　Purpurin.
Diamine Scarlet B.
Dianthine.
Erica B.
,,　　G.
Geranine G.
,,　　2 B.
St. Denis Red.

OXYKETONE COLOURS.

Alizarin Maroon (Al and Sn mordant).

NATURAL COLOURING MATTERS.

Cochineal (Al mordant).
Kermes (Al mordant).

Class IV.—Fast Colours.

TRIPHENYLMETHANE COLOURS.
Violamine A 2 R.

INDULINES.
Azo Carmine.

AZO COLOURS.
Acid Colours—
    Azo Acid Magenta B.
       ,,   ,,   G.
    ,,   Coccin 2 R.
    ,,   Fuchsine G.
    ,,   ,,   B.
    Brilliant Croceïn M O O.
      ,,   ,,   9 B
    Chromotrope 6 B cryst.
      ,,   . 8 B ,,
      ,,   10 B ,,
    Cloth Red No O B.
      ,,   B.
      ,,   G.
    Coccinin.
    Cochineal Red A.
    Cotton Scarlet N T.
    Croceïn Scarlet 3 B.
      ,,   ,,   7 B.
      ,,   3 B.
      ,,   A Z.
    Fast Ponceau B.
    Milling Red F G G.
      ,,   F R.
    Orseillin B B.
    Palatine Scarlet.
    Phœnix Red A.
    Ponceau 4 G B.
      ,,   2 G.
      ,,   R T.
      ,,   S extra.
      ,,   6 R.
    Wool Scarlet R.

OXYKETONE COLOURS.
Purpurin (Al mordant).

NATURAL COLOURING MATTERS.
Lac Dye (Al mordant).
Munjeet (,,   ).

Class V.—Very Fast Colours.

AZO COLOURS.
Acid Colours—
    Chromotrope 2 R cryst.
      ,,   2 B ,,

Direct Cotton Colours—
    Diamine Fast Red F.

OXYKETONE COLOURS.
Alizarin Bordeaux B (Al Sn mordant).
    ,,   ,,   G (,,   ).
    ,,   ,,   2 G (,,   ).
    ,,   (Al mordant).
    ,,   Turkey-Red (Al mordant) on cotton.
Anthrapurpurin (Al mordant).
Flavopurpurin (,,   ).
Nitroalizarin (Zn mordant).

NATURAL COLOURING MATTERS.
Chay Root (Al mordant).
Cochineal (Sn mordant).
Kermes Scarlet (Sn mordant).
Lac Dye (Sn mordant).
Madder (Al mordant).
Mang-kudu   (Al Sn mordant).
Morinda Root (,,   ).

ORANGE AND YELLOW DYES.

Class I.—Very Fugitive Colours.

TRIPHENYLMETHANE COLOURS.
Uranine.

DIPHENYLMETHANE COLOURS.
Auramine.

AZO COLOURS.
Basic Colours—
    Chrysoidine.

Direct Cotton Colours—
    Direct Orange R.
      ,,   ,,   R R.
      ,,   Yellow A S C.
      ,,   ,,   T S.
    Mimosa Yellow.
    Primuline Orange.

Terra-cotta F.
Thiazol Yellow.

ACRIDINE COLOURS.
Acridine Orange R extra.
      ,,   N O.
Benzoflavine.
Phosphine.

NITRO COLOURS.
Aurantia.
Brilliant Yellow.
Naphthol Yellow.
    ,,   ,,   S.
Picric Acid.

THIOBENZENYL COLOURS.
Primuline.
Thioflavine T.
    ,,   S.

NATURAL COLOURING MATTERS.
Annatto.
Coscinium fenestratum.
Evodia meliæfolia.
Gardenia Florida.
Saffron.
Tesu (Al mordant).
Turmeric.
Young Fustic (Al mordant).

Class II.—Fugitive Colours.

AZO COLOURS.
Acid Colours—
    Metanil Orange.
    Orange R.
        ,,   I.
    Phenoflavine.

Basic Colours—
    New Phosphine G.
    Tannin Orange.

Direct Cotton Colours—
    Benzo Orange R.
    Cloth Brown R.
        ,,   ,,   G.
        ,,   Orange.
    Nitrophenine.
    Salmon Red.
    Toluylene Brown G.
        ,,   Orange R.

QUINOLINE COLOURS.
Quinoline Yellow.

NATURAL COLOURS.
Flavin (Al mordant).
Jackwood (Al Sn mordant).
Kamála (Al mordant).
Old Fustic (Sn mordant).
Persian Berries (Sn mordant).
Quercitron Bark (,,   ).
Tesu (Cr mordant).

ARTIFICIAL MORDANT DYE.
Anthracine (Cr mordant).

Class III.—Moderately Fast Colours.

TRIPHENYLMETHANE COLOURS.
Aurotin.

AZO COLOURS.
Acid Colours—
    Acid Yellow O O.
    Azo Flavine S.
    Benzo Orange R.
    Brilliant Orange G.
    Cloth Orange R.
        ,,   G.
    Cotton Yellow.

Curcumein.
Dimethylaniline Orange.
Diphenylamine Orange.
Fast Yellow N.
Metanil Orange.
    ,,   Yellow.
Orange G T.
    ,,   H.
    ,,   III.
Primuline Yellow.
Resorcinol Yellow.
Tropaeolin X.

Direct Cotton Colours—
    Benzo Orange R.
    Brilliant Orange G.
    Carbazol Yellow.
    Congo Orange G.
        ,,   R.
    Cotton Yellow G.
        ,,   Orange R.
        ,,   ,,   G.
    Salmon Red.
    Toluylene Orange R.

MORDANT COLOURS.
Mordant Yellow.

NATURAL COLOURING MATTERS.
Jackwood (Cr mordant).
Morinda Root.
Weld (Al mordant).

Class IV.—Fast Colours.

AZO COLOURS.
Acid Colours—
    Acid Yellow.
    Brilliant Yellow S.
    Fast Yellow.
    Milling Orange O O.
        ,,   Yellow.
Direct Cotton Colours—
    Chrysamine R.
        ,,   G.
    Chrysophenine.
    Cresotine Yellow R.
        ,,   ,,   G.
    Diamine Yellow U.
    Oriol Yellow.
    Titan Yellow R.
        ,,   ,,   Y.

Mordant Colours—
    Chrome Orange.
        ,,   Yellow.
    Yellow for wool A F.

AZOXY COLOURS.
Chloramine Orange.
Diamine Orange D.
Direct Orange 2 R.

Palatine Orange.

Nitrazine Yellow.
Tartrazine.

Alizarin Yellow A (Cr mordant).
Galloflavin   (,,   ).

Persian Berries (Cr mordant).
Weld (Sn mordant).

Class V.—Very Fast Colours.

Acid Colours—
    Orange G G.

Mordant Colours—
    Alizarin Yellow R   (Cr mordant).
    ,,   ,,   G G W (,,   ).
    Anthracene Yellow C (,,   ).
    Diamond Yellow G   (,,   ).
    ,,   ,,   R   (,,   ).
    Flavazol   (,,   ).
    Gambine Yellow   (,,   ).

Direct Cotton Colours—
    Brilliant Yellow.
    Carbazol Yellow.
    Chloramine Yellow.
    Chrysamine G.
    ,,   R.
    Cresotin Yellow.

Diamine Gold.
Hessian Yellow.
Terra-cotta R.

Curcumin S.
Diamine Fast Yellow.
Direct Yellow G.
    ,,   3 G.
Mikado Orange, 3 R O.
    ,,   ,,   G O.
    ,,   Yellow.
    ,,   Gold Yellow 2 G.
    ,,   ,,   4 G.
    ,,   ,,   6 G.

Alizarin   (Sn mordant).
    ,,   S   (,,   ).
    ,,   S S (,,   ).
    ,,   S S S (Sn mordant).
    ,,   Orange W (Al and Sn mordant).
Anthrapurpurin (Sn mordant).
Flavopurpurin   (,,   ).
Purpurin   (,,   ).

Chay Root (Sn mordant).
Flavin (Al and Sn mordant).
Madder   (Sn mordant).
Morinda Root (,,   ).
Munjeet   (,,   ).
Old Fustic   (Cr, Al, Sn mordant).
Quercitron Bark (,,   ).
Sophora Japonica (Al mordant).
Weld (Cr, Al, Sn mordant).
Xanthaurin.

GREEN DYES.

Class I.—Very Fugitive Colours.

Basic Colours—
    Aldehyde Green.
    Capri Green.
    Iodine Green.
    Methylene Green.
    Solid Green 3 B.

Natural Colouring Matters—
    Lo-kao.

Class II.—Fugitive Colours.

Acid Colours—
    Fast Green extra.
    Guinea Green B.
    ,,   ,,   B V.
    Helvetia Green.

Light Green S F (blue shade).
    ,,   ,,   ,,   (yellow shade).
Basic Colours—
    China Green.
    Ethyl Green cryst.
    Imperial Green cryst.
    Methyl Green.
    Solid Green G G.
    ,,   ,,   Y Y O.

Mordant Colours—
    Chrome Green (Cr).

Basic Colours—
    Azine Green T O.

Direct Cotton Colours—
    Columbia Green.

Class III.—Moderately Fast Colours.

TRIPHENYLMETHANE COLOURS.

Acid Colours—
  Alkali Green,
  Milling Green.
  Wool Green S.

AZO COLOURS.

Direct Cotton Colours—
  Diamine Green B.

Mordant Colours—
  Azo Green (Cr).

Class IV.—Fast Colours.

Direct Cotton Colours—
  Benzo Olive.

Mordant Colours—
  Diamond Green (Cr).

Class V.—Very Fast Colours.

TRIPHENYLMETHANE COLOURS.

Mordant Colours—
  Cœruleïn (Cr).

OXYKETONE COLOURS.

Mordant Colours—
  Alizarin Green S W (Cr).

QUINONEOXIME COLOURS.

Mordant Colours—
  Dark Green (Fe).
  Dioxine (Fe).
  Gambine B (Fe).
  ,,   R (Fe).
  ,,   Y (Fe).
  Naphthol Green B (Fe).

BLUE DYES.

Class I.—Very Fugitive Colours.

TRIPHENYLMETHANE COLOURS.

Basic Colours—
  New Victoria Blue.
  Night Blue.
  Victoria Blue B.
  ,,   ,,   R.
  ,,   ,,   4 R.

AZO COLOURS.

Direct Cotton Colours—
  Brilliant Benzo Blue 6 B.
  Chicago Blue 6 B.
  Diamine Blue 6 G.
  Diamine Sky Blue.

OXAZINE COLOURS.

Basic Colours—
  Capri Blue.
  Cresyl Blue.
  Nile Blue.
  New Methylene Blue G G.

Acid Colours—
  Fluorescent Blue.
  Gallanilic Indigo P S.

SAFRANINE COLOURS.

Basic Colours—
  Neutral Blue.

THIAZINE COLOURS.

Basic Colours—
  Gentianine,
  Methylene Blue B.
  New Methylene Blue N.
  Thionine Blue G O.
  Toluidine Blue.

Class II.—Fugitive Colours,

TRIPHENYLMETHANE COLOURS.

Acid Colours—
  Cyanol, extra.

Basic Colours—
  Glacier Blue.
  Turquoise Blue.
  ,,   ,,   2 B.

AZO COLOURS.

Acid Colours—
  Azo Acid Blue B.

Direct Cotton Colours—
  Azo Blue.
  Azo Navy Blue.
  Benzo Azurine G.
  ,,   ,,   3 G.
  ,,   Blue 3 B.
  ,,   Cyanine 3 B.
  ,,   ,,   R.
  ,,   Red Blue G.
  ,,   ,,   K.
  Brilliant Metazurine O O O.
  Columbia Blue R.
  ,,   ,,   G.
  Diamine Blue B.
  ,,   ,,   2 B.
  ,,   ,,   3 B.
  ,,   ,,   B X.
  ,,   ,,   3 R.
  Direct Blue B.
  ,,   Blue Black B.
  Heligoland Blue 3 B.
  ,,   ,,   R.
  Indazurine.
  Indoin Blue 2 B.
  Metazurin B.

10

Naphthazurine.
Oxamine Blue 3 R.

OXAZINE COLOURS.

Acid Colours—
  Azine Blue.

Basic Colours—
  Metamine Blue B.
  Muscarin J.
  New Fast Blue F.
  ,,   ,,   H.

SAFRANINE AND INDULINE COLOURS.

Basic Colours—
  Basle Blue.
  Diphene Blue.
  Indazine M.
  Metaphenylene Blue B.

THIAZINE COLOURS.

Acid Colours—
  Thiocarmine.

NATURAL COLOURING MATTERS.

Acid Colours—
  Indigo Carmine.
  Indigo Purple.

Mordant Colours—
  Logwood (Al mordant).

Class II.—Moderately Fast Colours.

TRIPHENYLMETHANE COLOURS.

Acid Colours—
  Alkali Blue.
  ,,   ,,   6 B.
  ,,   ,,   D.
  ,,   ,,   R.
  Bavarian Blue D B F.
  ,,   ,,   D S F.
  Hoechst New Blue.
  Methyl Blue M B I.
  Patent Blue A.
  Soluble Blue.

Mordant Colours—
  Chrome Blue.

AZO COLOURS.

Acid Colours—
  Blue Black B.
  Indigo Blue powder.

Direct Cotton Colours—
  Benzo Black Blue C.
  ,,   ,,   ,,   R.
  ,,   Indigo Blue.
  Brilliant Azurine 5 G.
  ,,   Sulphon Azurine R.

Blue J C R.
Congo Fast Blue B.
  ,,   ,,   ,,   R.
Diamine Blue Black E.
Naphthyl Blue 2 B.
Sulphon Azurine.
  ,,   Cyanine.
  ,,   ,,   3 R.

OXAZINE COLOURS.

Acid Colours—
  Gallanilic Blue R.

Mordant Colours—
  Gallocyanin D H.

INDULINE COLOURS.

Acid Colours—
  Fast Blue B.
  Induline 3 B.
  ,,   N N.
  Indigen F liquid.
  Milling Blue.
  Naphthazine Blue.
  Naphthyl Blue.

Basic Colours—
  Indamine Blue N.
  Indophenine B.
  ,,   extra.
  Paraphenylene Blue R.
  Toluylene Blue B.

NATURAL COLOURING MATTERS.

Mordant Colours—
  Logwood (Cr, Fe, Cu).

Class IV.—Fast Colours.

TRIPHENYLMETHANE COLOURS.

Mordant Colours—
  Gallein (Cr).

Basic Colours—
  Gentiana Blue 6 B.

AZO COLOURS.

Acid Colours—
  Naphthol Blue Black.

OXAZINE COLOURS.

Mordant Colours—
  Gallamin Blue (Cr).

INDULINE COLOURS.

Acid Colours—
  Fast Blue 6 B, for wool.

Class V.—Very Fast Colours.

OXAZINE COLOURS.
Mordant Colours—
  Célestine Blue B (Cr).

THIAZINE COLOURS.
Mordant Colours—
  Brilliant Alizarin Blue G (Cr mordant).
    ,,   ,,   ,, R (,,   ).

OXYKETONE COLOURS.
Mordant Colours—
  Alizarin Blue S   (Cr mordant).
    ,,   ,, W X (,,   ).

Alizarin Cyanine Black G (Cr mordant).
  ,,   ,,   G   (,,   ).
  ,,   ,,   R   (,,   ).
  ,,   Indigo Blue S W (,,   ).
Anthracene Blue W G (,,   ).
  ,,   ,,   W R (,,   ).

Natural Colouring Matters—
  Vat Indigo Blue.

Additional Colours—
  Prussian Blue.

BROWN DYES.

Class I.—Very Fugitive Colours.

AZO COLOURS.
Direct Cotton Colours—
  Benzo Brown G.
    ,,   ,, 5 R.
  Cloth Brown (red shade).
  Hessian Brown M M.
  Titan Brown Y.
Basic Colours—
  Chrysoïdine A G.
    ,,   F F.
  Leather Brown R.
    ,,   ,,   V.

AZOXY COLOURS.
Direct Cotton Colours—
  Mikado Brown M.

Class II.—Fugitive Colours.

AZO COLOURS.
Acid Colours—
  Acid Brown G.
    ,,   ,, R.
  Alkali Brown.
  Fast Brown 3 B.
    ,,   ,, G.
  Naphthylamine Brown.
  Resorcin Brown.
  Sulphamine Brown.

Basic Colours—
  Chrome Brown B O.
    ,,   ,, R O.
    ,,   ,, R.
  Leather Brown.
    ,,   ,, O.
  Nut Brown.

Direct Cotton Colours—
  Azo Brown.
  Benzo Black Brown.
    ,, Brown.
    ,,   ,, B R.

Benzo Brown B.
  ,,   ,, N B.
Catechu Brown.
  ,,   ,, D D X.
  ,,   ,, D D D X.
Cloth Brown (yellow shade).
Congo Brown V B B.
Cotton Brown A.
  ,,   ,, N.
Diazochromine B S.
Direct Brown Y.
Hessian Brown B.
Sulphon Brown R.
  ,,   Dark Brown.
Toluylene Brown B.
  ,,   ,,   2 B O.
  ,,   ,,   M.
  ,,   ,,   R.
  ,,   ,,   V O.

Direct Cotton Colours developed—
  Diazo Brown G ⎫
    ,,   ,, R ⎬ Azotised and developed
    ,,   ,, V ⎪ with Beta-naphthol.
    ,,   ,, Y ⎭
  Zambesi Brown G ⎫ Azotised and devel-
    ,,   ,, 2 G ⎬ oped with Toluy-
               ⎭ lene Diamine.
  Diamine Brown V, azotised and developed
  with Phenylene Diamine.

NATURAL COLOURING MATTERS.
Mordant Colours—
  Barwood (Cr).
  Camwood (Cr).
  Catechu (Cr).
  Limawood (Cr).
  Sanderswood (Cr).
  Ventilago (Cr).

Class III.—Moderately Fast Colours.

AZO COLOURS.
Acid Colours—
  Azo Acid Brown.

Diamond Brown.
Fast Brown.

Direct Cotton Colours—
Benzo Dark Brown.
Congo Brown G.
　　　,,　　,,　R.
Diamine Bronze G.
　　,,　　Brown B.
　　,,　　　,,　M
　　,,　　Cutch.
Hessian Brown 2 B.
　　,,　　,,　2 B N.
Thiazine Brown G.
　　,,　　,,　R.

Direct Cotton Colours developed—
Naphthylene Violet, azotised and developed with Sodium Carbonate.

AZOXY COLOURS.

Direct Cotton Colours—
Mikado Brown 2 B.
　　,,　　　,,　B.
　　,,　　　,,　G.

NATURAL COLOURING MATTERS.

Mordant Colours—
Barwood (Cu) (Fe).
Camwood (Cu) (Fe).
Sanderswood (Cu) (Fe).
Ventilago (Cu) (Fe).

Class IV.—Fast Colours.

AZO COLOURS.
Direct Cotton Colours—
Direct Cotton Brown R.
Toluylene Brown G.

NATURAL COLOURING MATTERS.
Mordant Colours—
Cochineal (Cr).

Class V.—Very Fast Colours.

OXYKETONE COLOURS.
Mordant Colours—
Alizarin Bordeaux B　(Cr mordant).
　　,,　　　　,,　G　　(　,,　).
　　,,　　　　,,　G G　(　,,　).
　　,,　　Brown　　(　,,　).
　　,,　　Maroon　　(　,,　).
Anthracene Brown　　(　,,　).
Anthragallol　　　　(　,,　).

NATURAL COLOURING MATTERS.

Chay Root (Cr) (Cu) (Fe).
Cochineal (Cu) (Fe).
Lac Dye (Cr) (Cu) (Fe).
Madder (Cr) (Cu) (Fe).
Mang-kudu (Cr) (Cu) (Fe).
Morinda Root (Cr) (Cu) (Fe).
Munjeet (Cr) (Cu) (Fe).

ADDITIONAL COLOURS.
Oxidation Colour—
Chromogen I., oxidised with Bichromate of Potash.

BLACK DYES.

Class I.—Very Fugitive Colours.

AZO COLOURS.
Direct Cotton Colours—
Nyanza Black B.
Tabora Black R.

Acid Colours—
Violet Black.

Class II.—Fugitive Colours.

AZO COLOURS.
Acid Colours—
Anthracite Black R.
Azo Acid Black B.
　　,,　　　,,　G.
　　,,　Nigrine R.
Jet Black G.
Phenylene Black.
Wool Black.

Direct Cotton Colours—
Columbia Black B.
　　,,　　2 B.

Columbia Black R.
Direct Deep Black T.
Oxydiamine Black N.
　　,,　　　,,　S O O O.
Union Black S.

Direct Cotton Colours developed—
Diamine Black B H　} Developed with
　　,,　　B O　　} Fast Blue De-
　　,,　　R O O　} veloper A D.
Diazo Black B　} Developed with Beta-
　　,,　　H　　} naphthol.
　　,,　　R　　}

OXAZINE COLOURS.
Basic Colours—
Cotton Black.

NATURAL COLOURING MATTERS.
Mordant Colours—
Limawood (Fe).

Class III.—Moderately Fast Colours.

AZO COLOURS.

Acid Colours.
Acid Black B.
,,   2 B.
Jet Black R.
Naphthol Black B.
,,   3 B.
,,   6 B.
,,   4 R.
Naphthylamine Black.
,,   ,,   6 B.
,,   ,,   4 B.
New Victoria Black Blue.
,,   ,,   B.
,,   ,,   5 G.
Victoria Black Blue.
,,   B.
,,   C.
,,   5 G.

Direct Cotton Colours—
Benzo Black Blue G.
,,   ,,   5 G.
,,   ,,   R.
,,   Black.
,,   ,,   S extra.
Diamine Black H W.
,,   Jet Black S S.
,,   ,,   O O.

Direct Cotton Colours developed—
Diazo Brilliant Black B } Developed with
,,   ,,   R } Beta-naphthol.

Mordant Colours—
Chrome Black (Cr).
Diamond Black G A (Cr).
,,   N G (Cr).
,,   (Cr).

Basic Colours—
Diazine Black.

INDULINE COLOURS.

Acid Colours—
Brilliant Black E B.
Nigrisine.

Basic Colours—
Nigrisine T.

NATURAL COLOURING MATTERS.

Mordant Colours—
Cochineal (Fe).
Logwood (Cr) (Fe).

Class IV.—Fast Colours.

AZO COLOURS.

Mordant Colours—
Chrome Black.
Diamond Black.
,,   G A.
,,   N G.

OXYKETONE COLOURS.

Mordant Colours—
Alizarin Black S W (Fe).
,,   Bordeaux B (Fe).
,,   ,,   G (Fe).
Quinalizarin.

Class V.—Very Fast Colours.

OXYKETONE COLOURS.
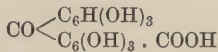
Mordant Colours—
Alizarin Bordeaux G G (Fe).

E

EAU DE JAVELLE *v.* POTASSIUM HYPO-CHLORITE.

ECHURIN. A mixture of *Picric acid* and *Nitroflavin.*

ECLIPSE RED *v.* BENZOPURPURIN 4 B.

EGG ALBUMIN *v.* ALBUMIN.

ELLAGIC ACID—

$$CO\begin{cases} C_6H(OH)_3 \\ C_6(OH)_3 . COOH \end{cases}$$

This acid occurs in *myrabolams, divi divi,* and other tannins. It is also produced by the action of arsenic acid and some other oxidising agents on tannic acid, or by the action of hydrochloric acid on many tannins. It may also be obtained by the hydrolysis of ellagitannic acid.

Ellagic acid is very slightly soluble in water or alcohol, and quite insoluble in ether. It produces with ferric chloride a green coloration, which rapidly becomes blue-black; but its most characteristic reaction is the production of a bright crimson colour when treated with nitric acid. An alkaline solution of ellagic acid is a powerful reducing agent.

ELLAGITANNIC ACID ($C_{14}H_{10}O_{10}$). This substance is very closely allied to tannic acid, being produced in an analogous manner by the decomposition, not of gall or sumac tannin, but of the tannins of *divi divi, myrabolams, pomegranate,* &c. It forms an amorphous mass, which is soluble in water or alcohol. Its aqueous solution gives precipitates with salts of antimony, lead, iron, &c., similar to those produced by tannic acid, which latter it resembles in most respects.

EMERALD GREEN (By.) *v.* BRILLIANT GREEN.

EMERY *v.* ALUMINIUM.

EMIN RED (Ber.). Red powder. Aqueous solution, red; alcoholic solution, yellow-red. Concentrated H_2SO_4, bluish-red; on dilution, becomes bright red.

Application.—An acid dye. Gives bright crimson shades on *wool* from an acid bath. When saddened with fluorchrome is fast to milling.

ENGLISH BROWN *v.* BISMARCK BROWN.

ENGLISH YELLOW *v.* VICTORIA YELLOW.

EOSAMIN B (Ber.). Brownish-red powder. Aqueous and alcoholic solution, bluish-red. Concentrated H_2SO_4, reddish-blue solution; on dilution, becomes bright bluish-red.

Application.—An acid colour. Dyes *wool* or *silk* bright bluish-red.

EOSINS (various) *v.* below; *v.* also ERYTHROSIN, PHLOXIN, ROSE BENGALE, CYANOSIN.

EOSIN A (B.). *Eosin* (F.), *Eosin G* (K.), *Eosin yellowish* (Ber.) (Br.S.), *Eosin G G F* (C.), *Eosin 3 J* (L.), *Eosin extra* (M.), *Eosin D H* (D. & H.), *Eosin soluble in water.* A phthaleïn colour. *Sodium or potassium salt of tetrabrom fluorescein.* 1874. Reddish-blue crystals or brownish-red powder, soluble in water with bluish-red colour, the dilute solution having a green fluorescence. In concentrated H_2SO_4, yellow solution; on dilution, yellow-red ppt.

Application.—Dyes *wool* and *silk* pinkish-red from a slightly acid bath (silk with a yellowish-red fluorescence). Dyes *cotton* mordanted with alum or lead, pink. Used also in making pink lakes for paper staining, &c.

EOSIN B N (B.). *Methyl eosin* (Ber.), *Safrosin* (S.C.I.) (B.) (Br.S.), *Eosin scarlet B* (C.), *Eosin B* (L.), *Scarlet J, J J, or V* (Mo.), *Eosin D H V* (D. & H.), *Eosin scarlet B B extra* (M.), *Lutecienne, Kaiser red.* A phthaleïn derivative. *Sodium or potassium salt of dibromdinitro fluorescein.* 1875. Brown crystalline powder, giving a yellowish-red solution in water which, when diluted, shows a green fluorescence. In concentrated H_2SO_4, brownish-yellow solution, which evolves bromine on heating; on dilution, brownish ppt.

Application.—*v.* EOSIN A.

EOSIN S (B.). *Eosin B B* (S.C.I.), *Rose J B* (*soluble in alcohol*) (S.C.I.), *Spirit eosin* (M.), *Ethyl eosin, Primrose* (*soluble in alcohol*). A phthaleïn derivative. *Potassium salt of tetrabrom fluorescein ethyl ether.* 1874. Brown powder or green crystals, insoluble in cold water, but soluble on boiling with a cherry-red colour with greenish-yellow fluorescence. In concentrated H_2SO_4, yellow solution, which evolves bromine on heating; on dilution, brownish-yellow ppt.

Application.—*v.* EOSIN A. Principally used in *silk* dyeing, producing a yellowish-red shade with weak fluorescence.

EOSIN J (B.). *Eosin bluish v.* ERYTHROSIN.

EOSIN 10 B (C.) *v.* PHLOXIN.

EOSIN SCARLET *v.* EOSIN B N.

EOSIN SPIRIT SOLUBLE *v.* EOSIN S and PRIMROSE (D. & H.).

EPSOM SALTS *v.* MAGNESIUM SULPHATE.

ERIE BLUE G G (Ber.). Blue powder. Aqueous solution, light blue; alcoholic solution, reddish-blue. Concentrated H_2SO_4, bright blue solution, becoming reddish-blue on dilution.

Application.—A direct cotton dye. Gives blue shades on *cotton* or *wool*. When afterwards treated with copper sulphate, the shade is duller but faster.

ERIKA B (Ber.). An azo compound.

| Dehydrothiometa-xylidine | — | Alpha-naphthol di-sulphonic acid. |

1888. Reddish-brown powder, soluble in water. In concentrated H_2SO_4, red solution; on dilution, red ppt.

Application.—A direct cotton colour. Dyes *cotton* red from an alkaline salt bath.

ERIKA G (Ber.). An azo compound.

| Dehydrothiometa-xylidine | — | Beta-naphthol gamma-disulphonic acid. |

Application.—*v.* ERIKA B.

ERIKA 4 G N (Ber.).

ERIOCHLORINE A, B, G B, B B (G.). Green dyes similar to above.

ERIOCYANINE A (G.). A rosaniline derivative. *Sodium salt of disulpho acid of tetramethyldibenzyl pararosaniline anhydride.* 1895. Violet powder. Aqueous solution, bright blue; alcoholic solution, reddish-blue. Concentrated H_2SO_4, dirty yellow solution; on dilution, bright green solution.

Application.—An acid colour, giving bright blues on *wool* or *silk*. Dyes also on chrome mordant.

ERIOCYANINE B (G.) is a similar colour, giving somewhat purer shades.

ERIOGLAUCINE A (G.). A rosaniline derivative. *Ammonium salt of tetrasulphonic acid of diethyldibenzyl diamidotriphenyl carbinol anhydride.* 1896. Reddish-blue powder. Aqueous and alcoholic solution, bright blue. Concentrated H_2SO_4, light yellow solution; on dilution, brownish-yellow, then olive-green.

Application.—An acid colour. Gives bright blue shades on *wool* or *silk*. Dyes also on chrome mordants.

ERIOGLAUCINE R B, B B, B, J, G B (G.). Similar colours to the above.

ERYTHRIN *v.* ORCHIL.

ERYTHRIN X (B.) *v.* PONCEAU 5 R (M.).

ERYTHRINE *v.* PRIMROSE (D. & H.).

ERYTHROBENZIN. An impure *Magenta.*

ERYTHROSIN (B.) (M.) (F.) (D. & H.) (Br. S.). *Erythrosin D* (C.), *Erythrosin B* (Ber.), *Pyrosin B* (Mo.), *Rose B* (S.C.I.), *Soluble Primrose* (D. & H.), *Eosin J* (B.), *Eosin bluish, Iodoeosin, Dianthine B.* A phthaleïn derivative. *Sodium or potassium salt of tetraiodofluorescein.* 1876. Brown powder, giving a cherry-red solution in water.

In concentrated H_2SO_4, brownish-yellow solution ; on dilution, brownish-yellow ppt.

Application.—*v.* Eosin A.

ERYTHROSIN B B *v.* Phloxin P.

ERYTHROSIN G (B.). *Pyrosin G* (Mo.), *Iodoeosin G, Dianthine G.* A phthaleïn derivative. *Sodium or potassium salt of di-iodofluorescein.* 1875. Yellowish-brown powder, soluble in water, with a cherry-red colour. In concentrated H_2SO_4, brownish-yellow solution, from which iodine separates on heating ; on dilution, yellow ppt.

Application.—*v.* Eosin A.

ETHER $(C_2H_5)_2O$. *Sulphuric ether.* Is prepared by heating a mixture of 9 parts of sulphuric acid with 5 parts of 90 per cent. alcohol to 135° C., at which temperature it is maintained, alcohol being slowly but continuously dropped into the mixture. The source of heat is *superheated* steam, direct fire being inadmissible. The vapour produced is condensed, and the distillate, after treatment with lime, is rectified to free it from alcohol and water.

Properties.—Ether is a colourless mobile liquid, having a pleasant characteristic smell. It boils at 35° C., and evaporates rapidly at the ordinary temperature. It does not mix with water, but 10 parts of water dissolve 1 part of ether. Alcohol is miscible with it in all proportions.

Ether is very inflammable, burning with a non-luminous flame. The vapour, mixed with air, explodes on ignition, and, owing to its great volatility, great care must be taken to avoid explosions. The vessels containing it must be kept away from gas jets and other lights.

Many organic compounds, notably hydrocarbons, fats, oils, and resins, readily dissolve in ether.

Analysis.—Pure ether undergoes no change when left in contact with caustic potash for twelve hours ; if kept cool and added carefully it dissolves in concentrated sulphuric acid without colour.

Ether is sometimes adulterated with *petroleum ether.* To determine its presence and approximate amount, Vitali * treats a moderate quantity of cooled ether with concentrated sulphuric acid in a graduated cylinder. The ether is taken up by the acid, and if it is pure there remains only a homogeneous liquid. If there remains a supernatant stratum, this is treated with a further quantity of sulphuric acid in order to find whether its volume is reduced. A portion of the supernatant liquid is then removed with a pipette and tested with a trace of iodine, which dissolves in petroleum ether with a violet colour, but with a brownish-yellow in ether.

Borrigter (*Archiv der Pharmacie*) mentions that ether often contains hydrogen peroxide.

* *Chemical News,* vol. liii., p. 69.

Such ether liberates iodine from potassium iodide, and colours potassium hydrate yellowish-brown. On distilling such ether there occurs at last an explosion, with the formation of a white vapour. Aldehyde is always found if hydrogen peroxide is present. Such samples, after prolonged treatment with potash, give no colouration with a fresh portion of the re-agent, and cease to decompose potassium iodide. In this manner ether may be purified from hydrogen peroxide, aldehyde, and water.

ETHYL ALCOHOL *v.* Alcohol.

ETHYL BLUE B F (M.). A basic dye, similar in character to Indamine Blue (*q.v.*).

ETHYL EOSIN *v.* Eosin S (B.).

ETHYL GREEN *v.* Methyl Green.

ETHYL GREEN (Ber.) *v.* Brilliant Green.

ETHYL PURPLE 6 B *v.* Ethyl Violet.

ETHYL VIOLET (B.) (L.). *Ethyl purple 6 B* (S.C.I.). A rosaniline derivative.

Hexamethyl pararosaniline hydrochloride.

1883. Green crystalline powder, soluble in water with a violet-blue colour. In concentrated sulphuric acid, brownish-yellow solution, which becomes green on dilution.

Application.—A basic colour. Dyes *wool* and *silk* bluish-violet from a neutral bath. *Cotton* is mordanted with tannic acid and tartar emetic.

ETHYLENE BLUE (O.) *v.* Methylene Blue.

EXTRACTING *v.* Cotton (Cellulose).

F

FABRICS, ANALYSIS OF TEXTILE, *v.* Textile Fabrics.

FABRICS, FIREPROOF, *v.* Incombustible Fabrics.

FADING OF COLOURS *v.* Dyes, Action of Light on.

FARINA *v.* Sizes.

FAST ACID BLUE B (By.). Reddish-blue powder. Aqueous solution, reddish-blue ; alcoholic solution, bright blue. Concentrated H_2SO_4, brownish-red solution ; on dilution, becomes reddish-blue, then blue.

Application.—An acid colour. Dyes *wool* violet-blue.

FAST ACID BLUE R (M.). *Violamine R* (M.). A phthaleïn derivative. *Sodium salt of sulphonic acid of diparaphenitidyl metaamidodichlor phenol phthaleïn.* 1889. Dark violet powder, soluble in water. In concentrated H_2SO_4, dark claret-red solution ; on dilution, red-violet solution, then precipitates as bluish flocks.

Application.—An acid colour. Dyes *wool* and *silk* violet-blue from an acid bath.

FAST ACID MAGENTA B (By.). An azo dye.

Aniline — *Amidonaphthol disulphonic acid H.*

Dark brown powder. Aqueous solution, bright red ; alcoholic solution, bluish-red. Concentrated H_2SO_4, bright red ; on dilution, orange-red, then pink.

Application.—An acid colour. Dyes *wool* and *silk* magenta-red from an acid bath.

FAST ACID PONCEAU (D. & H.). *Acid ponceau* (D. & H.). An azo dye.

Beta-naphthylamine mono-sulphonic acid *— Beta-naphthol.*

Scarlet-red powder, soluble in water. In concentrated H_2SO_4, magenta-red solution ; on dilution, brown ppt.

Application.—An acid colour. Dyes *wool* and *silk* scarlet from an acid bath.

FAST ACID RED A (M.). An acid colour.

FAST ACID VIOLET A 2 R (M.). *Violamine R* (M.). A phthaleïn colour. *Sodium salt of diorthotolylmetaamido phenol phthaleïn sulphonic acid.* 1888. Red powder, soluble in water with a violet colour. In concentrated H_2SO_4, yellowish-red solution ; on dilution, the colour changes to bluish-red, and a precipitate is formed.

Application.--An acid colour. Dyes *wool* and *silk* reddish-violet. Fast to light and alkali.

FAST ACID VIOLET B (M.). *Violamine B* (M.). A phthaleïn colour. *Sodium salt of diphenylmetaamido phenol phthaleïn sulphonic acid.* 1888. Dark violet powder, soluble in water. In concentrated H_2SO_4, reddish-yellow solution ; on dilution, first becomes violet, then precipitates as blue flocks.

Application.—v. FAST ACID VIOLET A 2 R.

FAST ACID VIOLET 10 B (By.). A rosaniline derivative. *Sodium salt of tetramethyl ethylbenzyl pararosaniline disulphonic acid.* 1892. Grey powder, giving a reddish-violet solution in water. In concentrated H_2SO_4, orange-yellow solution, which becomes greenish-yellow on dilution.

Application.—An acid colour. Dyes *wool* and *silk* violet-blue from an acid bath.

FAST AZO GRANAT (M.). A brownish-red produced upon cotton by padding with *beta-naphthol* and developing with *amidoazo toluol.* (*v.* AZO DYES ON COTTON.)

FAST BLACK (L.). An oxamine derivative, produced by the action of *nitroso-dimethyl aniline hydrochloride upon meta-oxy diphenylamine.* 1889. Black powder or paste, soluble in water with a violet colour. In concentrated H_2SO_4, black solution, becoming violet-black on dilution.

Application.—A basic dye, suitable only for cotton. Dyes *cotton* mordanted with tannin and iron, black.

FAST BLACK B (B.). Obtained by action of *sodium sulphide upon dinitronaphthalene.* 1898. Black-blue paste, insoluble in water or alcohol. In concentrated H_2SO_4, slightly soluble with a dirty green colour.

Application.—Dyes *cotton* direct from a cold, concentrated alkaline (caustic soda) bath jet black ; fast to acids.

FAST BLACK B S (B.). Obtained by action of alkali on *Fast black B.* 1894. Blue-black paste, giving a violet solution in water.

Application.—Dyes *cotton* or *silk* jet black direct from a cold, concentrated aqueous solution.

FAST BLUE (Br.S.) *v.* ALKALI BLUE.

FAST BLUE B (Ber.) (By.) (M.). A soluble induline. *v.* INDULINE.

FAST BLUE FOR COTTON (Ber.) *v.* NEW BLUE R (C.).

FAST BLUE 2 B FOR COTTON (Ber.) (P.) *v.* NEW BLUE B (C.).

FAST BLUE 6 B FOR WOOL (Ber.). A soluble induline of specially bright and pure shade. *v.* INDULINE.

FAST BLUE BLACK (L.). Identical with, or closely allied to, *Fast black* (L.) (*q.v.*).

FAST BLUE GREENISH (B.). A soluble induline. *v.* INDULINE.

FAST BLUE R FOR COTTON (Ber.) (M.) *v.* NEW BLUE R (C.).

FAST BLUE 2 R and 3 R (M.) *v.* NEW BLUE R.

FAST BLUE 3 R (C.). A soluble induline. *v.* INDULINE.

FAST BLUE R SOLUBLE IN SPIRIT (Ber.). An insoluble induline. *v.* INDULINE SPIRIT SOLUBLE.

FAST BORDEAUX O (M.) *v.* CLOTH RED B (O.).

FAST BROWN (M.). *Fast brown O N T* (M.). An azo dye.

Xylidine monosulphonic acid *Alpha-naphthol.* *Xylidine monosulphonic acid*

1879. Dark brown powder, soluble in water. In concentrated H_2SO_4, violet solution, becoming red on dilution.

Application.—An acid colour. Dyes *wool* and *silk* brownish-red from an acid bath. Used also in lake making.

FAST BROWN (By.). An azo colour.

Naphthionic acid *Resorcinol.* *Naphthionic acid*

1881. Dark brown powder, soluble in water. In concentrated H_2SO_4, dark red solution ; on dilution, dark brown ppt. with dirty reddish-brown solution.

Application.—An acid colour. Dyes *wool* brown from an acid bath.

FAST BROWN 3 B (Ber.).   An azo dye.

Beta-naphthylamine sul- — Alpha-naphthol.
phonic acid Br

1882.   Brown powder, soluble in water.   In concentrated H_2SO_4, blue solution ; on dilution, reddish-violet ppt.
Application.—An acid colour.   Dyes *wool* brown from an acid bath.

FAST BROWN G (Ber.) *v.* ACID BROWN (D.).

FAST BROWN N (B.) *v.* NAPHTHYLAMINE BROWN.

FAST COTTON BLUES *v.* NEW BLUE R and B.

FAST COTTON BROWN R (G.) *v.* POLY-CHROMINE B.

FAST GREEN *v.* DARK GREEN (B.), also MALACHITE GREEN.

FAST GREEN (By.).   *Fast green extra* (By.). *Fast green extra blue* (By.).   A rosani-line derivative.   *Tetramethyldibenzyl para-rosaniline disulphonate of soda.*   1885.   Dark bluish-green crystalline powder, soluble in water.   In concentrated H_2SO_4, yellowish-red solution ; on dilution, first pale then dark bluish-green solution.
Application.—An acid colour.   Dyes *wool* or *silk* green from an acid bath.

FAST GREEN EXTRA (By.) *v.* above.

FAST GREEN J (Mo.) (P.) *v.* BRILLIANT GREEN.

FAST GREEN M (D. & H.).   Produced by the action of *aniline* upon *Muscarin* (D. & H.).   1894.   Copper-brown powder, insoluble in water or alcohol, but soluble in acetic acid. In concentrated H_2SO_4, brownish-violet solution, becoming orange on dilution.
Application.—A basic colour.   Dyes tannin-mordanted *cotton* dark green.

FAST MARINE BLUE (O.) *v.* NEW BLUE B (C.).

FAST MARINE BLUE R M and M M (K.) *v.* NEW BLUE B (C.).

FAST MARINE BLUE G M (K.) *v.* NEW BLUE R (C.).

FAST MYRTLE GREEN *v.* DARK GREEN (B.).

FAST NEUTRAL VIOLET B (C.).   An azine colour.   *Ethyldimethyl ethyl safranine chloride.*   1880.   Bronzy powder, giving a reddish-violet solution in water.   In concentrated H_2SO_4, reddish-grey solution, becoming in turn blue, blue-violet, and red-violet on dilution.
Application.—A basic dye.   Tannin-mordanted *cotton* is dyed fast blue-violet from a neutral bath.

FAST NEW BLUE FOR COTTON *v.* PARAPHENYLENE BLUE R (D.).

FAST PINK FOR SILK (D. & H.) *v.* MAGDALA RED.

FAST PONCEAU B (B.) *v.* PONCEAU 3 R B (Ber.).

FAST PONCEAU 2 B (B.).   *Ponceau S extra* (Ber.).   An azo dye.

Amidoazo benzene di- — Beta - naphthol di-
sulphonic acid   sulphonic acid R.

1880.   Brown powder, giving a magenta-red solution in water.   In concentrated H_2SO_4, blue solution ; on dilution, yellowish-red.
Application.—An acid colour.   Dyes *wool* red from an acid bath,

FAST RED (Ber.) (D. & H.) (Lev.).   *Fast red E* (B.) (By.), *Fast red S* (M.), *Acid car-moisin.*   An azo dye.

Naphthionic acid — Beta-naphthol sulphonic
acid S.

1878.   Reddish-brown powder, giving bluish-red solution in water.   In concentrated H_2SO_4, violet solution, becoming red on dilution.
Application.—An acid colour.   Dyes *wool* red from an acid bath.

FAST RED (L.) (F.) *v.* FAST RED A.

FAST RED A (B.) (Ber.) (By.) (Lev.) (C. R.).   *Fast red A F* (K.), *Fast red O* (M), *Rocelline* (D. & H.) (C.) (S.C.I.) (G.) (P.), *Brilliant red* (Sch.), *Cerasine, Orcellin 4, Rauracienne, Rubidin.*   An azo dye.

Alpha-naphthylamine — Beta-naphthol.
sulphonic acid

1877.   Brownish-red powder, slightly soluble in cold water, easily in hot water, with a scarlet colour.   In concentrated H_2SO_4, violet solution ; on dilution, yellowish-brown ppt.
Application.—An acid colour.   Dyes *wool* red from an acid bath.

FAST RED B (B.) *v.* BORDEAUX B (Ber.).

FAST RED B T (By.) (Lev.) (D. & H.). An azo dye.

Alpha-naphthylamine — Beta-naphthol
sulphonic acid S.

1878.   Brown powder, soluble in water, with a magenta - red colour.   In concentrated H_2SO_4, blue solution, becoming magenta - red on dilution.
Application.—An acid colour.   Dyes *wool* and *silk* claret-red from an acid bath.   Used in lake making.

FAST RED C (B.).   *Azo rubin* (Lev.),*Azo rubin A* (C.), *Azo rubin S* (Ber.), *Azo acid rubin* (D.), *Carmoisin* (B.) (By.), *Brilliant carmoisin O* (M.).   An azo dye.

Naphthionic acid — Alpha-naphthol sul-
phonic acid N W.

1883.   Brown powder, giving magenta-red solution in water.   In concentrated H_2SO_4, violet solution, becoming magenta - red on dilution.
Application.—An acid colour.   Dyes *wool* brownish-red from an acid bath.

FAST RED D (B.) *v.* AMARANTH (C.).

FAST RED E (B.) (By.), *v.* FAST RED (Ber.).

FAST RED E B (B.) *v.* AMARANTH (C.).

FAST RED N S (By.) *v.* AMARANTH (C.).
FAST RED O (M.) *v.* FAST RED A (B.).
FAST RED PR EXTRA (Ber.). 1899. An acid dye, producing crimson shades on wool.
FAST RED S (M.) *v.* FAST RED (Ber.).
FAST SCARLET B (K.).   An azo dye.

Amidoazo benzene sul-   Beta-naphthol sul-
  phonic acid   phonic acid S.

1879.   Red-brown powder, giving a scarlet solution in water.   In concentrated H_2SO_4, blue solution, becoming red on dilution.
Application.—An acid colour.   Dyes *wool* and *silk* scarlet from an acid bath.
FAST VIOLET (D. & H.) *v.* GALLOCYANIN.
FAST VIOLET BLUE SHADE (By.). An azo dye.

Alpha-naphthylamine $\Big\langle$ *Paratoluidine sul-
phonic acid.
Beta-naphthol sul-
phonic acid S.*

1882.   Greenish - brown powder, giving a violet solution in water.   In concentrated H_2SO_4, dirty green solution ; on dilution, violet ppt.
Application.—An acid colour.   Dyes *wool* bluish-violet from an acid bath.   May also be applied on chrome mordant.
FAST VIOLET RED SHADE (By.).   An azo dye.

Alpha-naphthylamine $\Big\langle$ *Sulphanilic acid.
Beta-naphthol sul-
phonic acid S.*

1882.   Dark green metallic-looking powder, soluble in water with a violet colour.   In concentrated H_2SO_4, dirty greenish-blue solution ; on dilution, first bright greenish-blue solution, then red-violet ppt.
Application. — v. FAST VIOLET-BLUE SHADE.
FAST WOOL BLUE (G.) *v.* ALPINE BLUE (G.).
FAST YELLOW (B.) (By.) *v.* ACID YELLOW.
FAST YELLOW (B.).   *Fast yellow R* (K.), *Yellow W* (By.). An azo dye. *Sodium salt of amidoazotoluol disulphonic acid.*   1878. Brownish-yellow powder, soluble in water. In concentrated H_2SO_4, yellowish - brown solution, becoming magenta-red on dilution.
Application.—An acid colour.   Dyes *wool* and *silk* in acid bath reddish-yellow.
FAST YELLOW (Br.S.) *v.* ORANGE 4.
FAST YELLOW G (D. & H.) (K.) *v.* ACID YELLOW.
FAST YELLOW GREENISH (D.) *v.* ACID YELLOW.
FAST YELLOW R (K.) *v.* FAST YELLOW (B.).
FAST YELLOW S (C.) *v.* ACID YELLOW.
FATTY ACID DETERMINATIONS *v.* LUBRICATING OILS (*Analysis*).
FERRIC SALTS *v.* IRON.
FERROUS SALTS *v.* IRON.

FIBROIN *v.* SILK.
FINE BLUE *v.* SPIRIT BLUE.
FISETIN *v.* FUSTIC (YOUNG).
FIXING AGENTS.   This term is applied, mainly in cotton dyeing, to certain substances employed in converting the soluble compounds used in mordanting into an insoluble form *upon the fibre.*   The fixing agents act mainly as precipitants ; for example, in mordanting cotton with aluminium, the fibre, after impregnation with basic alum solution, may pass into a " fixing bath " containing a solution of *sodium carbonate, phosphate, arsenate,* or *silicate,* when insoluble compounds are produced on the cotton.
The acid mordants—tannic or oleic acids— (*v.* MORDANTS) also require to be " fixed," and in this case certain metallic salts are employed as fixing agents.   When cotton is steeped in tannin solution, or is saturated with soap, no actual fixation of tannic or oleic acid occurs ; on washing the whole would be removed.   By treatment with a metallic salt solution, however, insoluble metallic tannates or oleates are produced on the fibre.
The chief salts used as fixing agents for tannic acid are compounds of *antimony, tin,* and *iron,* the latter being only applicable for dark shades on account of the dark colour of tannate of iron.   For oleic acid, *aluminium* salts are usually employed as fixing agents.
FLASHING POINT *v.* LUBRICATING OILS.
FLAVANILINE (M.).   A quinolin dye. *Hydrochloride of para-amido phenyl lepidine.* 1881.   Orange-red crystalline powder, giving a yellow solution in water.   In concentrated H_2SO_4, pale yellow solution with blue fluorescence.
Application.—A basic colour.   Dyes tannin-mordanted *cotton* yellow.
FLAVANILINE S (M.).   *Sodium salt of sulphonated flavaniline.* 1881. Orange-yellow powder, soluble in water.   In concentrated H_2SO_4, colourless solution, becoming yellow on dilution.
Application.—An acid colour.   Dyes *wool* or *silk* greenish-yellow from an acid bath.
FLAVAURINE.   An old yellow dye, allied to ANILINE ORANGE.
FLAVAZOL (Ber.).   Closely allied to, if not identical with, GAMBINE YELLOW.
Application.—A mordant dye.   Giving a yellow on chrome-mordanted wool.
FLAVIN *v.* QUERCITRON BARK.
FLAVINDULINE (B.).   An azine dye. Obtained by the action of *phenanthrene quinone* on *ortho-amido diphenylamine.* 1893. Orange-red powder, giving an orange-yellow solution in water.   In concentrated H_2SO_4, bluish-red solution, becoming yellow on dilution.
Application.—A basic colour.   Dyes tannin-mordanted *cotton* yellow.
FLAVOPHENIN (B.) *v.* CHRYSAMINE G.

FLAVOPURPURIN. *Alizarin R G, G 1* (B.), *Alizarin S D G* (M.), *Alizarin X* (By.), *Alizarin C A* (B. A. Co.). An anthracene derivative. *Trioxyanthraquinone.* 1876.

Application.—v. ALIZARIN.

FLAX or LINEN. Flax is the most important of the bast fibres, and ranks second only to cotton amongst vegetable fibres in general utility. The term *flax* is now usually applied to the plant, while *linen* is used to designate the separated fibre.

Flax is produced by various species of *Linum*, of which *Linum usitatissimum* is much the most important. It is an annual, growing 2 to 3 feet high, and of very wide distribution. It is, however, chiefly imported into Britain from Russia, although the best quality is produced in Belgium. Flax is still grown to a considerable, although decreasing, extent in Ireland.

Linen fibre is obtained from the plant by the following series of operations :—

Rippling.—This consists in drawing the stems through coarse combs to remove the seeds (linseed). The seeds are subjected to hydraulic pressure, yielding *linseed oil.* The dry stem at this stage contains only 20 to 25 per cent. of pure fibre.

Retting.—The bast fibres are cemented to the woody portion of the stem in such a permanent manner that a drastic treatment is necessary for their separation. The retting process consists in subjecting the plant to a putrefactive process, which is carried out in various ways, which may be distinguished as—

(a) Retting in stagnant water.
(b) Retting in running water.
(c) Dew retting.
(d) Special processes.

(a) *Retting in stagnant water* consists in steeping the bundles of dried flax in tanks until the fibrous portion separates more or less from the woody core. This is brought about by a fermentative process said to be due to a special micro-organism (*Bacillus amylobacter*). Many other putrefactive processes are also induced, and the tanks evolve a most nauseous smell. If care is not taken to stop the process at the proper time, the fibre itself is rotted, and, therefore, it is usual to remove the flax before the operation is complete and subject to *dew retting*.

Retting in stagnant water is chiefly carried out in Russia and Ireland, and fibre thus treated has a dark colour.

(b) *Retting in Running Water.*—This occupies from ten to twenty days, and produces a lighter coloured fibre. The flax is packed into frames, or crates, and immersed in the stream of water ; the fermentation, which sets in after two or three days, being much less active than that induced by stagnant water. The danger of "over-retting" is thus much less. This process is largely adopted in France, Belgium, and Holland.

(c) *Dew Retting.*—As its name implies, this consists in exposing the flax to the action of the dew. The fibre is kept moist, if necessary, and turned over occasionally, the process occupying six to ten weeks. This produces the best quality fibre, but is more costly than water retting.

(d) *Special Processes.*—To accelerate the retting process warm water treatment is sometimes resorted to, the flax being steeped in tanks at a temperature of 25° to 35° C. This *warm water retting* occupies two days only, but stains the fibre considerably.

W. Dogny proposes to treat the flax for twenty to forty minutes in closed vessels with water at 150° C., and then expose it for twenty minutes to the action of dry high-pressure steam. This process is said to yield excellent results under careful supervision. R. Baur steeps the flax in water until no further yellow colour is extracted, and then steeps a second time for two to three days in water containing 3 per cent. of hydrochloric acid.

After retting by any process, the fibre is well washed, and then dried. The quality of the fibre depends greatly upon the success of the retting process.

Breaking.—This is the first of a series of mechanical operations which have for their object the removal of the woody portion of the stem as completely as possible.

Breaking is done either by hand or by machinery, and by means of fluted rollers or otherwise the brittle woody matter is crushed into small pieces.

Scutching.—In this the woody matter is beaten out, the pliable fibre remaining unaffected.

Hackling consists in combing the fibre to remove the residue of woody matter and the short or broken fibre. The combed or hackled flax, which is technically known as *flax-line*, is the raw material of the linen manufacturer.

Tow is the short fibre produced during hackling, and is used for caulking the seams of wooden vessels, &c.

Counts.—In linen yarns the counts indicate the number of *leas* to the pound. One *lea* consists of 300 yards.

PHYSICAL STRUCTURE AND PROPERTIES.

Linen differs materially from cotton as regards physical structure and properties. The ultimate fibre cells are 25 to 40 mm. in length and 0·012 to 0·026 mm. in breadth, but in *flax-line* a large number of individual fibres are aggregated together to produce a fibre from 12 inches to 30 inches in length, the individual fibres seldom being separated.

The chief physical properties of pure linen fibre are its high degree of lustre, its great

strength, and its extreme whiteness. It is a better conductor of heat than cotton, and hence linen articles feel colder to the touch than cotton. Air-dried linen contains from 4 to 8 per cent. of hygroscopic moisture.

Chemical Composition.

Raw linen fibre, or *flax-line*, contains from 15 to 30 per cent. of impurities, which consist largely of pectic matters, with some wax, woody matter, &c. These are removed during the bleaching operations. The pure fibre consists of *cellulose*, which is indistinguishable chemically from that of cotton.

Chemical Properties.—Towards reagents generally linen behaves in a manner similar to cotton. In bleaching, it requires longer and more complicated treatment owing to the difficulty of removing the large amount of impurity which the raw fibre contains.

Linen is more difficult to dye than cotton, probably on account of the difference in the physical structure of the two fibres.

FLOUR *v.* Sizes.

FLUORESCEÏN is *Resorcin phthaleïn.* *Uranin* is the sodium salt of *Fluoresceïn.* 1871. *Fluoresceïn* is a brown powder, insoluble in water but soluble in alcohol. *Uranin*, yellowish-brown powder, easily soluble in water with a yellow colour and (in dilute solution) intense green fluorescence. The fluorescence is absent in strong solutions. In concentrated H_2SO_4, yellow solution without fluorescence ; unchanged on dilution.

Application. — Dyes *silk* yellow from a slightly acid bath. Chiefly employed for making *Eosins*.

FLUORESCENT BLUE (L.) (S. C. I.). *Resorcin blue, Iris blue* (B.). An oxamine derivative. *Ammonium salt of tetrabrom resorufin.* 1880. Brownish-red paste, with green lustre, giving a violet solution in water with a green fluorescence. In concentrated H_2SO_4, the dry colour gives a blue solution : on dilution, first violet solution, then brown precipitate.

Application.—Dyes *silk* blue with a brownish fluorescence. Used also in preparation of ortho chromatic photographic plates.

FORMALDEHYDE, H. CHO. *Formalin.*

Preparation. —Formaldehyde is prepared by passing a stream of air mixed with methyl alcohol vapour over a heated copper spiral. The vapours yield on condensation a liquid containing 30 to 40 per cent. of formaldehyde. On evaporating, the solution becomes more concentrated, with comparatively little loss of formalin.

Properties.—The aqueous solution of formalin has a penetrating smell and reduces ammoniacal silver solutions with the formation of a silver mirror. It combines with ammonia to form *hexamethyleneamine*—

$$6 H . CHO + 4 NH_3 = (CH_2)_6 N_4 + 6 H_2 O.$$
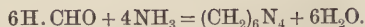
On evaporating a concentrated solution of formalin it polymerises to solid *paraformaldehyde* $(H . CHO)_n$.

H. Silbermann[*] states that, after weighting, soupled silk can be dyed a full black with logwood by treating the silk for two hours in a bath with 3 per cent. commercial formalin, and subsequently dyeing with logwood in a soap bath.

Analysis.—F. C. J. Bird[+] takes advantage of the action of ammonia on formaldehyde (as shown in the above equation) to produce hexamethyleneamine for the quantitative estimation of this substance.

(1) Titrate the solution with standard ammonia, using rosolic acid to indicate the end of the reaction.

(2) Add excess of standard ammonia and titrate back with standard acid.

(3) Add excess of ammonia, evaporate to dryness, and weigh the hexamethyleneamine formed, calculating the formaldehyde from the above equation.

These methods are only accurate when acetaldehyde and acids are absent.

G. Romijn[‡] recommends the following process, based on the property formaldehyde exhibits of combining with potassium cyanide when solutions containing these substances are mixed. The addition product can reduce alkaline silver nitrate solution in the cold, but if the solution be kept acid with nitric acid then, when the aldehyde is in excess, one molecule of formaldehyde combines with one molecule of potassium cyanide, the excess of the latter precipitating silver cyanide from the silver nitrate present.

FORMALIN *v.* Formaldehyde.

FORMYL VIOLET S 4 B (C.). *Acid violet 6 B* (G.), *Acid violet 4 B extra* (By.). A rosaniline derivative. *Acid sodium salt of tetraethyldibenzyl pararosaniline disulphonic acid.* 1890. Bluish-violet powder, soluble in water. In concentrated H_2SO_4, orange-yellow solution, becoming olive-green, then green, and finally blue on dilution.

Application.—An acid colour. Dyes *wool* bluish-violet from an acid bath.

FORMYL VIOLET 6 B, 8 B, and 10 B (C.) are similar products to the above.

FREEZING MIXTURES. When matter passes from the solid to the liquid state a large quantity of heat is absorbed, and this fact is taken advantage of for the purpose of obtaining artificial cold.

The substances used should be in a comparatively fine state of division, the mixing should take place quickly, and the mixture must be placed in vessels having little conducting power.

[*] *Journ. Soc. Chem. Ind.*, 1897, p. 139.
[+] *Pharm. Journ.*, 1896, vol. lvii., pp. 269-271.
[‡] *Journ. Soc. Chem. Ind.*, 1897, p. 367.

The following freezing mixtures are readily prepared and cause a considerable reduction of temperature :—

2 parts of ice and 1 part of salt ;

5 parts of commercial hydrochloric acid and 8 parts of crystallised sulphate of soda ;

equal parts of crystallised ammonium nitrate, soda crystals, and water.

FRENCH GALLS *v.* GALLNUTS.

FUCHSIA (S.C.I.). *Methylene violet 2 R A and 3 R A* (M.). An azine derivative. *Dimethyl safranine chloride.* 1887. Black powder, slightly soluble in water, with a red-violet colour. In concentrated H_2SO_4, green solution ; on dilution, first blue, then violet-red.

Application.—A basic colour. Dyes tannin-mordanted *cotton* reddish-violet. Used principally in *calico* printing.

FUCHSIACINE. An old name for impure MAGENTA.

FUCHSINE (B.) (By.) (C.) (L.) (D.) (K.) (D. & H.) (M.) (O.) *v.* MAGENTA.

FUCHSINE S (B.) *v.* ACID MAGENTA.

FUCHSINE ACIDE *v.* ACID MAGENTA.

FUCHSINE SCARLET. A mixture of *Magenta* and *Auramine*.

FULLER'S EARTH is an argillaceous earth, usually of a greenish-brown or slate-blue colour occurring in Surrey, Kent, Bedfordshire, and elsewhere. It may be regarded as a hydrated silicate of alumina. It is found in beds in association with the chalk and oolite. Occasionally it is nearly white in colour. Its specific gravity is 2·0, and it is very soft and possesses an earthy fracture and a dull appearance. It falls to pieces in water, but does not become plastic. Fuller's earth adheres to the tongue very slightly, and has a greasy feel. It possesses the power of absorbing grease or oil in a remarkable degree. It is used in the fulling or cleansing of cloth.

FUR *v.* WOOL.

FUSEL OIL *v.* AMYL ALCOHOL.

FUSTIC. *Old Fustic, Yellow Wood.* This is much the most important of the natural yellow dyestuffs, being still largely used in wool dyeing. There appears to be no record of the actual date of the introduction of old fustic to European dyes, but it was certainly in use about the end of the seventeenth century.

Origin.—Old fustic is, or has been, also known under the various names of *Cuba wood, yellow wood, yellow Brazil wood,* and *dyers' mulberry.* It is the heart wood of the tree variously called *Morus tinctoria* or *Maclura tinctoria ;* natural order, *Urticaceæ.* This tree, which grows in the West Indies, tropical America, and India, has oblong taper leaves and an edible fruit. It grows to a considerable size, often attaining a height of from 50 to 70 feet, and, in addition to its use as a dyestuff, the wood is sometimes employed

in cabinet work. It is imported in small logs, and is hard, and of a brownish-yellow colour. Several qualities are distinguished, the distinctive names usually indicating the district of exportation—viz., Cuba, Tampico, Carthagena, Jamaica, &c. Cuba fustic is the most esteemed variety.

Colouring Matters in Old Fustic.—The colouring matters contained in fustic were first investigated by Chevreul,[*] who isolated two distinct compounds, to which the names *Morin* or *moric acid* and *Maclurin* or *moritannic acid* were later given by Wagner.[†] Hlasiwetz and Pfanndler[‡] have also investigated these products. *Morin* or *moric acid* is the principal colouring matter. When pure it forms pale yellow lustrous needles, having the composition $C_{12}H_8O_5H_2O$. It is insoluble in cold water, but dissolves slightly on boiling. It is easily soluble in alcohol or alkalies. When fused with caustic potash it yields *phloroglucin*, which is also one of the products obtained by like treatment from *quercetin* (*v.* QUERCITRON BARK). There are, indeed, many points of resemblance between morin and quercetin, and in all probability there is an intimate chemical relationship between the two colouring matters.

Maclurin, or *moritannic acid,* has the composition $C_{13}H_{10}O_6$ (possibly $C_{13}H_8O_5H_2O$). When pure it forms pale yellow needles, and is easily soluble in water, alcohol, or ether. An interesting decomposition is brought about when maclurin is heated with zinc and sulphuric acid. A red colour is developed, which rapidly changes to orange, the solution then containing *phloroglucin* and *machromin.*

Machromin is soluble in water with a yellow colour, which changes to blue by atmospheric oxidation. Ferric chloride produces a brilliant purple coloration. Concentrated sulphuric acid dissolves machromin with an orange colour, the solution becoming green on heating.

The diazo benzene compound of maclurin is sold commercially under the name of "fustine," or "wool yellow."

Commercial Preparations of Fustic.—Fustic, like logwood, is sold as *chipped* or *rasped wood,* and as a solid or liquid extract. After chipping or grinding, the wood is usually "matured" or "aged" in the same way as logwood—*i.e.,* it is spread in layers on a floor, and, after being well moistened, it is allowed to remain several weeks, the mass being re-mixed at intervals.

In the case of logwood, the essential action of the ageing process is the oxidation of *hæmatoxylin* into *hæmatein,* but no similar change takes place in the case of fustic, and

[*] *Lecous de Chemie Appliquée à la Teinture,* vol. ii., p. 150.

[†] *Journ. für Prakt. Chem.,* vol. ii., 1882.

[‡] *Ann. der Chem. und Pharm.,* vol. cxxvii., p. 351.

the only benefit the process appears to confer is the somewhat incidental one of thoroughly soaking the wood and thus rendering the colouring matter more susceptible to extraction in the dye-bath.

Fustic extracts are manufactured in the same way as logwood extracts (*v.* LOGWOOD). The liquid extract is usually said to be of a strength of 51° Tw., but consisting as it does of a lower layer of insoluble morin, upon which rests a pasty solution of maclurin, the true specific gravity is not easy to determine.

THE EXAMINATION OF FUSTIC EXTRACT.

Fustic extract is often adulterated with *dextrin, molasses, zinc sulphate, glycerine, starch sugar, alum, turmeric extract, aniline dyestuffs,* and *alizarin orange.*

The presence of large quantities of *zinc sulphate* manifests itself by the turbidity of the solution. The determination of small quantities of zinc sulphate is more difficult, and the ash of the extract brought to a white heat will often cause errors. Extracts which contain zinc will, in feebly acid or neutral dye-baths, cause the material to become streaky, owing to the separation of a zinc lake. Pure extract of fustic dissolves in water in the proportion of 1 to 300, with a light yellow colour.

L. Bruhl * gives the following methods for the examination of fustic extract :—

Zinc sulphate is determined by drying the extract, then gently charring and extracting the finely-powdered mass with dilute boiling nitric acid. The solution is then tested for zinc.

Alum may also be tested for in the nitric acid solution.

The determination of *extract of turmeric* is based upon the property of this extract to dye wool directly without a mordant, which property fustic does not possess. The best material for these tests is *well-scoured* woollen cashmere ; any fat present will act as a mordant. 1 grm. of the extract is dissolved in 50 c.c. hot water, diluted with half a litre of cold distilled water, and poured into a porcelain dish. The cashmere is then entered, the liquid is brought to the boil in a quarter of an hour with constant stirring, and after boiling five minutes the material is taken out and well washed. If then its colour is pure white, no trace of turmeric was present. If the colour of the tissue is yellow, then adulteration with turmeric or aniline dyestuffs has taken place. The cashmere is extracted with alcohol, and the latter evaporated to a few c.cm. A part of it is used for testing for aniline dyestuffs possibly present ; if there are none only the adulteration with turmeric is possible. To make sure, however, in cases

* *Journ. Soc. Dyers and Col.*, 1889, p. 124.

of suspected adulteration with alum, in which case fustic would dye directly, the following reactions are carried out :—

Reagent.	Turmeric.	Fustic.
Stannous chloride.	Reddish precipitate.	Light yellow precipitate.
Lead acetate.	Chestnut brown.	Reddish-yellow.
Ferric sulphate.	No precipitate. Solution coloured brown.	Black precipitate. Solution coloured brown ; . afterwards turning olive-green.
Caustic alkalies.	Brown coloration.	Dark orange coloration, but no precipitate.
Mineral acids.	Red coloration ; no precipitate ; on diluting the coloration disappears and the dyestuff separates out in yellow flakes.	Light yellow precipitate.

Extract of quercitron does not dye wool directly, and alum is but a feeble mordant for quercitron upon wool, producing only a poor shade, whilst fustic under similar conditions gives a deep yellow colour. Stannous chloride in the presence of tartaric, oxalic, or hydrochloric acid, dyes in combination with quercitron a deep orange upon wool, while fustic gives delicate shades. On these facts the following method of detecting quercitron is based :—

A slip of white woollen cashmere, 10 cm. by 20 cm., dyed in a mixture of 0·5 grm. extract, 0·2 grm. alum, 0·5 grm. stannous chloride, 0·5 grm. oxalic acid in 1 litre water, if contrasted with a similar dyeing trial with an extract adulterated with quercitron, will give different results, which difference manifests itself by the greater intensity of colour of the adulterated extract. If now a swatch of the same size is dyed in the extracts under comparison, but with alum mordant alone, the adulterated extract will give weaker colourings than the pure extract of fustic. Although this method does not yield quantitative results, with some practice the percentage can be determined approximately.

Moritannic acid, or maclurin, has the decided character of a tannic acid, therefore extracts of fustic give all the reactions peculiar to tannic acids.

Molasses, dextrin, &c., are determined as in logwood extracts (*q.v.*).

Fustic extracts, similarly to those of logwood, are very frequently adulterated. The best qualities usually contain about 5 per

cent. of adulteration, while poor qualities may contain as much as 40 per cent.

For the production of fustic extract pure fustic is not generally employed, but a mixture of about 95 per cent. fustic and 5 per cent. quercitron bark. As the best fustic yields at most only 15 per cent. solid extract, while quercitron bark often gives 30 per cent. solid extract, it follows that most commercial fustic extracts offered as pure contain from the beginning 10 per cent. admixture.

Havres, as well as German, extract works generally use for "best" quality the following composition :—

1000 litres	extract of fustic,	25° B.=675		dry
100	,, zinc sulphate solution,	30° B.= 37		extract.
50	,, molasses solution,	42° B.= 41		

Consequently, the dry extract of 753 kilos. contains 78 kilos. of adulterants, or 10 per cent. of admixture. If it is now considered that the fustic extract from the commencement contained 10 per cent. quercitron, the total adulteration contained in "best" extract would amount to about 20 per cent.

Determination of the Amount of Colouring Matter in Fustic Extract.—10 grms. of the extract, dried at 110° C., are extracted with absolute alcohol ; the remaining insoluble matter consists of extractive substances which contaminate the extract. The alcoholic solution is mixed with three-quarters its volume of hot water, whereby the morin is almost completely precipitated. The precipitate is washed several times with hot water, and the washing water added to the filtrate. On evaporating the latter to one-half its volume a large quantity of the maclurin separates out, and the remainder on the addition of hydrochloric acid. The total weight of morin and maclurin thus obtained, after drying at 100° C., constitutes the percentage of dyestuff contained in the extract. The method is sufficiently correct for technical purposes.

DYEING PROPERTIES OF MORIN AND MACLURIN.

As has been already noted, these two colouring matters both exist in old fustic and its extract, and since they behave very differently in dyeing, the following brief summary of their properties will be of interest.* The experiments were made with the pure colouring matters :—(1) Neither morin nor maclurin are easily affected by oxidising agents, which probably accounts for the fact that the dyeing power of fustic which has undergone the "ageing" process is not at all increased thereby.

(2) With *chromium* mordant, *morin* produces fuller and brighter shades than *maclurin*, the former being yellowish-olive-green, and

* Gardner's *Wool Dyeing*, vol. ii.

the latter drab in colour. The presence of chalk in the dye-bath has little influence upon the result.

With *aluminium* mordant, again, the *morin* alone is useful, giving a bright orange-yellow colour, whereas *maclurin* gives only a pale drab. The presence of a calcium salt in the dye-bath is, however, essential to the production of the orange-yellow shade, and it appears to be a normal constituent of the morin-aluminium colour lake.

On the contrary, with *iron* mordant *maclurin* is much the more valuable of the two colouring matters, giving the olive-green shade which is produced by old fustic with this mordant, whereas *morin* yields light browns only. With this mordant, as with aluminium, the addition of a lime salt to the dye-bath is necessary.

Maclurin behaves in many respects like a tannin matter, giving a precipitate with glue or gelatine and a strong coloration with iron salts. It is a somewhat powerful acid, decomposing carbonates or acetates, and dissolving metallic iron with considerable facility.

Application.—Fustic is the most important of the natural yellow dyes. It is mainly used in wool dyeing in conjunction with chrome mordant, with which it yields brownish-olive or old gold colours. It forms a constituent of a large series of brown, olive, and other compound shades, and is added to logwood blacks to neutralise the bluish tone of the logwood.

FUSTIC, YOUNG.—This dyestuff, which is now practically obsolete, is the wood of *Rhus cotinus*, a species of sumac tree growing principally in the West Indies, but also in Southern Europe. The wood is imported in the form of small logs and branches, which, after being rasped or ground, are used in the same manner as other dyewoods. *Young fustic* is of much greater antiquity as a dye than the now much more important *old fustic*, and the use of the terms "young" and "old" in connection with these woods is irrational and misleading, since there is no connection, botanical or otherwise, between them.

Colouring Matters of Young Fustic.—Since the leaves of *Rhus cotinus* constitute one variety of sumac, young fustic contains, as might be expected, a large amount of tannin matter. It is also said to contain three colouring matters—one yellow, one brown, and one red. The yellow colouring matter was isolated by Chevreul, who gave it the name of *fustin*, subsequently changed to *fisetin*. It may be prepared by extracting the ground wood with boiling water, from which the colouring matter is precipitated by basic acetate of lead. The lead compound is decomposed by dilute sulphuric acid, and

the solution, after filtering off the lead sulphate, is evaporated to crystallisation. The crude product may be purified by re-crystallisation from dilute alcohol.

Application.—Young fustic is now practically obsolete. With tin mordant it produces bright reddish-orange shades on wool, which are, however, very fugitive to light.

FUSTINE (Wood & Bedford) *v.* PATENT FUSTINE, also FUSTIC.

G

GALENA *v.* LEAD.

GALLACETOPHENONE *v.* ALIZARIN YELLOW C.

GALLAMINE BLUE (G.) (By.). An oxamine derivative, obtained by the action of *nitroso dimethylaniline on gallaminic acid.* 1889. Grey paste, soluble in water with a greenish colour. In concentrated H_2SO_4, purplish-blue solution; on dilution, deep red.

Application. — A mordant dye. Dyes chrome-mordanted *wool* blue.

GALLANILINDIGO P (D. & H.). Produced by the action of *aniline* upon the condensation product of *nitroso dimethylaniline* with *tannin-anilide.* 1890. Blue paste with coppery lustre, insoluble in water. In concentrated H_2SO_4, reddish-violet solution; on dilution, yellowish-red.

Application. — A mordant dye. Dyes chrome-mordanted *wool* blue.

GALLANILINDIGO P S (D. & H.). Ammonium salt of sulphonic acid of previous dye. 1891. Coppery blue paste, soluble in water. In concentrated H_2SO_4, violet solution, becoming yellowish-red on dilution.

Application.—An acid mordant dye. Dyes *wool* blue from a slightly acid bath. May be used with or without chrome mordant.

GALLANIL GREEN (D. & H.). *Solid green G* (D. & H.). Action of nitric acid on Gallanilindigo. 1895. Black-brown-bronzy powder, slightly soluble in water with a bluish-green colour. In concentrated H_2SO_4, cherry-red solution; on dilution, brown ppt.

Application. — A mordant dye. Dyes chrome-mordanted *wool* green.

GALLANIL VIOLET B S (D. & H.). Action of *nitroso dimethylaniline* on *tannin anilide* and combination of the product with *sodium bisulphite.* 1889. Black liquid, slightly soluble in water with a blue colour. In concentrated H_2SO_4, greyish-red solution, becoming dull claret-red on dilution.

*Application.* — A mordant dye. Dyes chrome-mordanted *wool* reddish-purple.

GALLAZIN A (D. & H.). Oxidation of the condensation product of *Gallocyanin* with *Beta-naphthol sulphonic acid S.* 1893. Brown paste, soluble in water with difficulty. In concentrated H_2SO_4, blue solution; on dilution, blue ppt.

Application. — A mordant dye. Dyes chrome-mordanted *wool* blue.

GALLEÏNE (D. & H.) (By.) (Fi.). *Galleïne A* (M.), *Galleïne W* (B.), *Alizarin violet*, *Anthracene violet.* A phthaleïn derivative. *Oxidation product of pyrogallol phthaleïn* 1870. Violet paste or dark green metallic crystalline powder, slightly soluble in cold water with a scarlet-red colour. In concentrated H_2SO_4, reddish-yellow solution; unchanged on dilution.

Application. — A mordant dye. Dyes chrome-mordanted *wool* or *silk* violet. Used in making *Coeruleïne.*

GALLIC ACID. *Trioxybenzoic acid.*

$$\left(C_6H_2 \begin{cases} OH\ (1) \\ OH\ (2) \\ OH\ (3) \\ COOH\ (5) \end{cases} \quad 2H_2O \right).$$
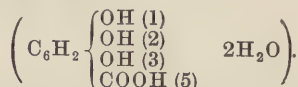
Gallic acid is produced by the hydrolysis of tannic acid, a decomposition which may be brought about either by fermentation or by heating with dilute acids or caustic alkalies. It may also be readily obtained synthetically from benzene or toluene.

Gallic acid is always found in small quantities in gall-nuts and sumac, and is probably there produced by the decomposition of tannic acid. It also exists in tea. It forms colourless, triclinic crystals, which become anhydrous when dried at 100° C. It decomposes at about 215° with formation of (principally) *pyrogallol* (pyrogallic acid).

$$C_6H_2 \begin{cases} (OH)_3 \\ COOH \end{cases} = C_6H_3(OH)_3 + CO_2.$$
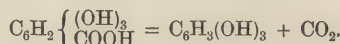
When heated quickly to 250°, *metagallic acid* is the chief product. Heated to 140° with sulphuric acid, *rufigallic acid* (hexaoxyanthraquinone), $C_{14}H_8O_8$, is formed, while a mixture of gallic and benzoic acids, or of gallic acid, phthalic acid, and zinc chloride, under the same conditions, yields *anthragallol*, $C_{14}H_8O_3$ (anthracene brown). Both rufigallic acid and anthracene brown are brown dyestuffs belonging to the anthracene (alizarin) series.

Gallic acid is soluble in 130 parts of cold or 3 parts of boiling water, also in 4 parts of alcohol, or 40 parts of ether. Its aqueous solution has an astringent taste and a slightly acid reaction; it reduces salts of silver and gold with precipitation of the metal, and has a slight reducing action on Fehling's solution. It is a mono-basic acid, and forms easily crystalline salts. Solutions of the alkaline gallates, like all alkaline salts of phenols, absorb oxygen with great avidity and become brown.

Ferrous salts produce a white precipitate with gallic acid in concentrated solution, this rapidly becoming blue, and depositing a black precipitate on exposure to air. *Ferric salts* produce at once a blue precipitate which

partially dissolves in excess of the reagent, producing a green solution.

Tartar emetic gives a white precipitate of antimony gallate.

Gallic acid is of little value in dyeing since it is only absorbed to a very slight degree by cotton. It also lacks the property of changing skin into leather, giving no precipitate with gelatine or albumen, nor with organic bases or starch.

Gallic acid is employed to a considerable extent in the making of certain coal-tar dyes —*e.g.*, *gallein*, *gallocyanin*, and *anthracene brown*. It is also used in photography and medicine.

GALLIPOLI OIL *v.* OLIVE OIL.

GALL-NUTS. These are distinguished as *Oak galls* and *Chinese galls*.

Oak Galls are produced by the puncture of the female gall-wasp, *Cynips gallæ tinctoriæ*, on the young buds of the small branches of certain species of oak (*Quercus infectoria*). In the puncture ovæ are deposited, round which an excrescence rapidly forms, this constituting the gall-nut. The insects gradually develop, and, on reaching maturity, puncture the gall-nut and escape. If gathered before the puncture takes place the galls are bluish or greenish in colour, and are the richest in tannic acid, the punctured galls being white or yellow in colour and much lighter in weight. Gall-nuts are approximately spherical and from 10 to 20 millimetres in diameter. The best variety are the so-called *Aleppo galls*, which are largely obtained from Persia; those from *Turkey* and the *Levant* are somewhat inferior, and *Italian*, *French*, and *German* galls contain considerably less tannic acid, the amount of which, in different varieties of galls, varies between 25 and 77 per cent.

Chinese and Japanese Gall-Nuts.—*Chinese galls* are produced upon the tender branches of *Rhus semialata*, a species of sumac, by the insect *Aphis Chinensis*. They are light in colour, hollow, and very irregular in shape, with pointed protuberances. They are considerably larger than oak galls, but the external walls being thin they are somewhat lighter.

Japanese galls are similar to Chinese in appearance, size, and weight. They are produced upon *Rhus japonica* or *R. Javanica*, and are considered somewhat superior to the Chinese variety. Both kinds are rich in tannin, of which they contain 60 to 75 per cent.

GALLOCYANIN B S (D. & H.). The sodium bisulphite compound of the following.

GALLOCYANIN D H (D. & H.). *Solid violet, Fast violet, Alizarin purple.* An oxazine derivative. Action of *nitroso dimethylaniline* on *gallic acid* in alcoholic solution. The commercial colour is the free base. 1881. Greenish crystalline paste, insoluble in water (B S is soluble). In concentrated H_2SO_4,

cornflower-blue solution, which changes to magenta-red on dilution.

Application. — A mordant dye. Dyes chrome-mordanted *wool* bright bluish-violet.

GALLOFLAVIN W (B.). Partial *oxidation* of *gallic acid* in aqueous or alcoholic solution. 1886. Greenish-yellow paste, insoluble in water. In concentrated H_2SO_4, reddish-yellow solution; on dilution, greyish precipitate.

Application. — A mordant dye. Dyes chrome-mordanted *wool* yellow.

GALLOTANNIC ACID *v.* TANNIC ACID.

GAMBIER *v.* CATECHU.

GAMBINE B (H.) *v.* DIOXINE (L.).

GAMBINE G (H.). *Gambine* (Ber.) (K.), *Alsace green J.* A nitroso compound. *Alphanitroso beta - naphthol.* 1875. Olive - green paste, soluble in water with a yellow colour. In concentrated H_2SO_4, dark brown solution; on dilution, brown precipitate.

Application.—A mordant dye. Dyes ironmordanted *wool* green; chrome - mordanted *wool* brown.

GAMBINE R (H.). A nitroso compound. *Beta-nitroso alpha-naphthol.* 1875. Greenish-yellow paste, slightly soluble in water. In concentrated H_2SO_4, reddish-brown solution; on dilution, yellow solution and brown ppt.

Application.—*v.* GAMBINE G.

GAMBINE YELLOW (H.). Light brown paste, slightly soluble in water with light yellow colour. Alcoholic solution, bright yellow. Concentrated H_2SO_4, yellowish-brown solution; on, dilution becomes yellow.

Application. — A mordant dye. Dyes chrome-mordanted *wool* olive-yellow.

GAMBOGE. Is a resin produced from the *Garcinia morella.* It dissolves in ammonia with a yellow colour, and this solution produces yellow and red colours with zinc, alumina, and lime mordants.

GARANCINE *v.* MADDER (*Preparations*).

GARNET (D. & H.) *v.* CARMINAPHTHE GARNET.

GARNET BROWN. *Isopurpuric acid.* An obsolete acid dye, obtained by the action of *potassium cyanide* on *picric acid.* 1859.

GENTIANA BLUE 6 B (Ber.). *Spirit blue* (B.) (By.) (L.) (Br. S.) (C. R.) (D.), *Spirit blue S F C* (K.), *Opal blue* (C.) (Br.S.), *Light blue* (P.), *Hessian blue* (L.), *Blue spirit soluble* (M.). A rosaniline derivative. *Hydrochloride, sulphate, or acetate of triphenyl rosaniline and para rosaniline.* 1860. *Hydrochloride* is a greyish-green powder, *sulphate or acetate* blue-violet powder. Insoluble in water, soluble in alcohol. In concentrated H_2SO_4, brownish-yellow solution; on dilution, blue ppt.

Application.—Dyes *wool* or *silk* blue from a slightly acid bath. Principally used for preparing *alkali* and *soluble* blues, and in the manufacture of spirit lakes.

11

GENTIANINE (G.). A thiazine derivative. *Zinc chloride double salt of dimethyl thionin.* 1886. Reddish-brown powder, soluble in water with a blue-violet colour. In concentrated H_2SO_4, yellowish-green solution; on dilution, first blue, then blue-violet.

Application.—A basic colour. Dyes tannin-mordanted *cotton* bright blue.

GERANINE 2 B (By.). Dark bluish-red powder. Aqueous solution, bluish-red; slightly soluble in alcohol. Concentrated H_2SO_4, bluish-red solution; on dilution, turns redder.

Application.—A direct cotton colour. Dyes unmordanted *cotton* bluish-crimson. Suitable also for *wool* and *silk*.

GERANINE G (By.). Brownish-red powder. Aqueous solution, bright red; alcoholic solution, duller. Concentrated H_2SO_4, bluish-red; on dilution, bright red, then orange-red.

Application.—A direct cotton colour. Dyes unmordanted *cotton* yellower shades than the above.

GERANIUM. An impure *Magenta* containing *Phosphine*.

GIROFLÉE (D. & H.). *Tannin heliotrope* (C.), *Heliotrope B and 2 B* (K.), *Methylene violet* (D. & H.). An azine derivative. *Chloride of dimethyl xylyl safranine.* Brown paste or greyish-green powder, soluble in water with a magenta-red colour. In concentrated H_2SO_4, green solution, which becomes blue and then red on dilution.

Application.—A basic colour. Dyes tannin-mordanted *cotton* reddish-violet.

GLACIAL ACETIC ACID *v.* ACETIC ACID.

GLADIOLIN O, I, II. Direct cotton red. Dyes similar to BRILLIANT CONGO G.

GLAUBER'S SALT *v.* SODIUM SULPHATE.

GLYCERIN, $C_3H_5(OH)_3$. Glycerin is a trihydric alcohol, occurring in small quantities in wine and beer, as a product of the alcoholic fermentation of sugar. The radical C_3H_5 (*glyceryl*) occurs in combination in most animal and vegetable fats and oils.

Preparation.—Glycerin is obtained chiefly as a by-product in the soap and candle industries. By whatever process the oils and fats are saponified glycerin is one of the resulting compounds, occurring in dilute solutions of varying purity, depending on the materials used for its separation. After purification from fat, &c., the dilute glycerin solutions are concentrated, and the residue distilled by means of superheated steam, the impurities remaining behind.

Properties.—Glycerin is a colourless syrupy liquid having a sweet taste. It is very soluble in water, and when anhydrous absorbs moisture from the air. It dissolves in alcohol, but is insoluble in ether. At 15° C. its specific gravity is 1·2650. It decomposes slightly on distilling alone, but can be purified, as mentioned above, by distillation in the presence of water vapour or under reduced pressure. Glycerin dissolves the alkalies, alkaline earths, and many metallic oxides, forming glyceroxides; for example, Monosodium glyceroxide, $NaC_3H_7O_3$, Calcium glyceroxide, $CaC_3H_6O_3$, &c.

The ethers of glycerin with palmitic, stearic, and oleic acids are important natural substances occurring in the majority of fats and oils. Glycerin is added on account of its hygroscopicity to print-colours, finishing materials, &c., to prevent them from drying.

Analysis of Glycerin. — The strength of glycerin is determined by means of the specific gravity. The coefficient of expansion of glycerin is 0·0006 for an increase of 1° C.

SPECIFIC GRAVITY OF GLYCERIN SOLUTIONS
At 150° C. (*Skalweit*).

Glycerin per cent.	Sp. Gr. Compared with Water at 15° C.	Glycerin per cent.	Sp. Gr. Compared with Water at 15° C.
0	1·0000	61	1·1599
2	1·0048	62	1·1628
6	1·0144	63	1·1657
8	1·0192	64	1·1686
10	1·0240	65	1·1715
12	1·0290	66	1·1743
15	1·0365	67	1·1771
20	1·0490	68	1·1799
25	1·0620	69	1·1827
30	1·0750	70	1·1855
31	1·0777	71	1·1882
32	1·0804	72	1·1909
33	1·0831	73	1·1936
34	1·0858	74	1·1963
35	1·0885	75	1·1990
36	1·0912	76	1·2017
37	1·0939	77	1·2044
38	1·0966	78	1·2071
39	1·0993	79	1·2098
40	1·1020	80	1·2125
41	1·1047	81	1·2152
42	1·1074	82	1·2179
43	1·1101	83	1·2206
44	1·1128	84	1·2233
45	1·1155	85	1·2260
46	1·1182	86	1·2287
47	1·1209	87	1·2314
48	1·1236	88	1·2341
49	1·1263	89	1·2368
50	1·1290	90	1·2395
51	1·1318	91	1·2421
52	1·1346	92	1·2447
53	1·1374	93	1·2473
54	1·1402	94	1·2499
55	1·1430	95	1·2525
56	1·1458	96	1·2550
57	1·1486	97	1·2575
58	1·1514	98	1·2600
59	1·1542	99	1·2625
60	1·1570	100	1·2650

Pure glycerin boils at 290° C., but a small addition of water lowers the boiling point considerably.

Estimation of Gum.—Alcohol is added to a weighed quantity of glycerin, in a tared basin (after standing twelve hours the gum will separate out), decant, wash with alcohol once, dry and weigh the residue.

Glucose, Cane Sugar, and Dextrin (Mason's method).—Three drops of glycerin are boiled with 110 drops of water, 1 drop of nitric acid, and 1 grm. of ammonium molybdate. In presence of any of the three mentioned substances the solution turns blue within two minutes. Gum-Arabic, milk-sugar, and glycerin give no reaction.

Treacle, when added to glycerin, may be detected according to Palm, by adding a few drops of nitric acid and evaporating on the water-bath. If the residue blackens, cane sugar is present; glycerin and grape sugar are not discoloured.

Glucose (grape sugar) is present if the solution turns brown on boiling with caustic potash solution. Fehling's solution is reduced on boiling with glucose solutions.

Lime is detected by means of ammonia and ammonium oxalate.

Chlorine may be detected by the addition of a little nitric acid and silver nitrate, a white precipitate being caused if chlorine be present.

Sulphuric acid is indicated if a turbidity is produced after acidifying with hydrochloric acid and adding barium chloride.

Ash.—A quantity of the sample is ignited, and the residue weighed.

Butyric Acid.—A peculiar butter-like odour is developed by this substance if present when a small amount of the glycerin is rubbed in the hand. If concentrated sulphuric acid be added to the glycerin in alcoholic solution, the pine-apple odour of butyric ether is observed.

Determination of Glycerin in Soap - lye Glycerin.—The method devised by Hehner [*] is the best. It is carried out as detailed below:—

(1) A standard solution of pure potassium bichromate containing 74·564 grms. of $K_2Cr_2O_7$, and 150 c.c. concentrated H_2SO_4 per litre. 1 c.c. = ·001 grm. glycerin.

(2) A solution of ferrous ammonium sulphate, containing about 240 grms. per litre. 1 and 2 are titrated against each other very carefully.

(3) A portion of the strong bichromate solution is diluted until its strength is exactly $\frac{1}{10}$ of No. 1.

About 1·5 grm. of crude glycerin is accurately weighed into a 100 c.c. flask, and sufficient oxide of silver added to precipitate the chlorine of the sodium chloride and oxidise the aldehydes present. After the addition of 5 or 10 c.c. of water the mixture is left to stand for ten minutes, after which a

* *Journ. Soc. Chem. Ind.,* 1889 p. 4.

slight excess of basic lead acetate solution is added and the liquid made up to 100 c.c., well shaken, and poured on a dry filter. 25 c.c. of the filtrate are transferred to a beaker, and 50 c.c. of 50 per cent. sulphuric acid, together with 50 c.c. of the strong bichromate solution. The beaker is placed in a bath of boiling water, and the water kept vigorously boiling for two hours. The excess of bichromate is then titrated back with an excess of the ferrous sulphate solution, the latter being eventually titrated with the dilute bichromate solution. Drops of potassium ferricyanide on a plate are used as an indicator. The titrations should all be carried out at the same temperature.

As one of the principal uses of glycerin in printworks is dissolving arsenious acid, R. Williams [*] uses the following test for determining the amount which a sample is capable of dissolving. A weighed amount of glycerin is heated together with a known excess of arsenious acid. The mixture is diluted with water and poured on a tared filter. After completely washing the undissolved portion, the filter and its contents are dried and weighed. The amount of arsenious acid dissolved is then found by subtracting the residue of arsenic from the amount originally taken. Good glycerin should dissolve about 6 lbs. of arsenic to the gallon.

GLYCINE BLUE (K.). An azo dye.

Benzidine sulphon$\Big\langle$ *Alpha-naphthyl glycin.*
$\quad\quad\quad\quad\quad$ *Alpha-naphthyl glycin.*

1891. Dark brown powder, soluble in water with a crimson-red colour. In concentrated H_2SO_4, blue solution; on dilution, violet ppt.

Application.—A direct cotton colour. Dyes *cotton* blue from an alkaline soap bath.

GLYCINE CORINTH (K.). An azo dye.

Benzidine$\Big\langle$ *Alpha-naphthol glycine.*
$\quad\quad\quad\quad$ *Alpha-naphthol glycine.*

1891. Brown powder, giving a bluish-red solution in water. In concentrated H_2SO_4, blue solution; on dilution, violet ppt.

Application.—A direct cotton colour. Dyes *cotton* brownish-red from an alkaline soap bath.

GLYCINE RED (K.). An azo dye.

Benzidine$\Big\langle$ *Alpha-naphthol glycine.*
$\quad\quad\quad\quad$ *Naphthionic acid.*

1891. Reddish-brown powder, giving a yellowish-red solution in water. In concentrated H_2SO_4, blue solution; on dilution, violet ppt.

Application.—A direct cotton dye. Dyes *cotton* red from an alkaline soap bath.

GOLD BROWN *v.* BISMARCK BROWN.
GOLD ORANGE (By.) (D.) *v.* ORANGE II.
GOLD ORANGE *v.* ORANGE III.

* *Journ. Soc. Chem. Ind.,* 1886, p. 73.

GOLD ORANGE FOR COTTON (D. & H.)
v. CHRYSOIDINE.

GOLD YELLOW (By.) *v.* RESORCIN
YELLOW.

GOLDEN ROD (*Hydrastis* or *Canadensis*)
has been used as a yellow dye for a consider-
able time. In conjunction with alum it pro-
duces a pure lemon yellow.

GRAY R and B (S.C.I.) *v.* INDULINE.

GRAY J and R (P.) *v.* METHYLENE GREY.

GREENISH BLUE (M.). A green shade
of *Alkali blue*.

GREEN GREASE *v.* ANTHRACENE.

GREEN POWDER = METHYL GREEN.

GREEN VERDIGRIS *v.* COPPER (BASIC
COPPER ACETATE).

GREEN VITRIOL *v.* IRON (FERROUS SUL-
PHATE).

GRENADINE. An impure *Magenta* con-
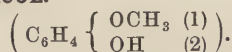taining *Phosphine*.

GRENAT. An impure *Magenta* containing
Phosphine.

GRENAT S (B.). An impure *Acid
magenta*.

GROUNDING BLACK FOR COTTON
(B). 1899. A direct cotton colour, suitable
for dyeing the cotton of union cloth without
much colouring the wool.

GUERNSEY BLUE. A low quality of
Alkali blue.

GUAIACOL.

$$\left(C_6H_4 \left\{ \begin{array}{ll} OCH_3 & (1) \\ OH & (2) \end{array} \right. \right).$$

This substance, the methyl ether of catechol,
is a constituent of wood tar, and is found in
small quantities in pyroligneous acid.

GUIGNET'S GREEN *v.* CHROMIUM
HYDROXIDE.

GUINEA GREEN B (Ber.). A triphenyl-
methane derivative. *Sodium salt of diethyl-
dibenzyl diamidotriphenyl carbinol disulphonic
acid.* 1883. Dark green non-lustrous pow-
der, soluble in water. In concentrated H_2SO_4,
yellow solution; on dilution, first yellowish-
red, then yellowish-green, and finally green.
Application.—An acid colour. Dyes *wool*
and *silk* green from an acid bath.

GUINEA GREEN B V (Ber.). The nitro
compound of the above. 1889. Bluish-green
powder, soluble in water. In concentrated
H_2SO_4, brown solution, becoming yellowish-
green on dilution.
Application.—An acid colour. Dyes *wool*
or *silk* green from an acid bath.

GUINEA RED 4 R (Ber.). Brownish-red
powder. Aqueous solution, yellowish-red;
alcohol, slightly soluble, bluish-red. In con-
centrated H_2SO_4, yellowish-red; unchanged
on dilution.
Application. — An acid colour. Gives
bright red shades on *wool* or *silk*.

GUINEA VIOLET 4 B (Ber.). Brown
powder. Aqueous solution, reddish-blue;

alcoholic solution, violet. Concentrated
H_2SO_4, brownish-yellow solution; on dilution,
becomes olive green, then bright blue.
Application.—An acid colour. Dyes *wool*
or *silk* bright bluish-violet.

GUM *v.* KINO.

GUMS *v.* THICKENERS.

GUN COTTON *v.* COTTON (ACTION OF
ACIDS).

GYPSUM *v.* CALCIUM SULPHATE.

H

HACKLING *v.* FLAX.

HÆMATEIN *v.* LOGWOOD.

HÆMATOXYLIN *v.* LOGWOOD.

HALF-WOOL BLACK *v.* UNION BLACK
(C.).

HARMALINE. An old name for impure
Magenta.

HAWTHORN BLOSSOM, WHITE *v.* YEL-
LOW WALLFLOWER.

HEATH (*Erica vulgaris*) contains a colour-
ing matter which dyes yellow in conjunction
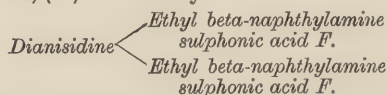with alum mordant.

HEAVY SPAR *v.* BARIUM SULPHATE.

HELIANTHINE (B.) *v.* ORANGE III.

HELIANTHINE (G.) *v.* AZO YELLOW.

HELIGOLAND BLUE 3 B (Noetzel). A
direct cotton blue, giving a reddish shade.

HELIOCHRYSINE. An obsolete nitro
compound. *Tetra nitro alpha-naphthol.* 1882.
An acid dye.

HELIOTROPE (B.). *Heliotrope B* (By.)
(Ber.) (L.). An azo dye.

Dianisidine $\left\{\begin{array}{l} \textit{Ethyl beta-naphthylamine} \\ \quad \textit{sulphonic acid F.} \\ \textit{Ethyl beta-naphthylamine} \\ \quad \textit{sulphonic acid F.} \end{array}\right.$
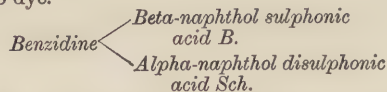
1887. Brown powder, giving a magenta-red
solution in water. In concentrated H_2SO_4,
blue solution; on dilution, bluish-violet ppt.
Application. — A direct cotton colour.
Dyes *cotton* reddish-violet from an alkaline
bath.

HELIOTROPE B and 2 B (K.) *v.* GIRO-
FLÉE.

HELIOTROPE 2 B (By.) (Ber.) (L.). An
azo dye.

Benzidine $\left\{\begin{array}{l} \textit{Beta-naphthol sulphonic} \\ \quad \textit{acid B.} \\ \textit{Alpha-naphthol disulphonic} \\ \quad \textit{acid Sch.} \end{array}\right.$

1892. Dark grey powder, giving a reddish-
violet solution in water. In concentrated
H_2SO_4, blue solution; on dilution, reddish-
violet ppt.
Application.—A direct cotton colour. Dyes
cotton violet from an alkaline bath.

HELIOXANTHIN *v.* ORANGE IV.

HELVETIA BLUE (G.) *v.* BAVARIAN
BLUE D B F.

HELVETIA GREEN (S.C.I.). An obsolete acid green.

HEMP. This fibre is the bast of the *Cannabis sativa*, an annual closely allied to the hop. The plant grows from 4 to 6 feet in height, and, while indigenous to Central and Western Asia, is now grown in almost all temperate and tropical countries. It is cultivated chiefly in Russia, Hungary, Germany, France, Italy, and the southern portion of the United States, the best quality being grown in Italy. In India it is mainly grown on account of the narcotic resin which the flowers and seeds contain. The fibre is extracted from the plant by retting, breaking, scutching, &c., as in the case of flax (*q.v.*).

Hemp is mainly used in the manufacture of ropes, &c., which are extremely durable and strong. It is very seldom bleached or dyed.

The ultimate fibres of hemp resemble those of linen in their appearance under the microscope. They have a diameter of 0·015 to 0·021 mm., and consist essentially of cellulose.

The retted fibre contains about 70 per cent. of cellulose and 30 per cent. of ligno cellulose, pectic and other extractive matters, moisture and ash.

The seed of the plant yields a valuable oil.

HENNA is of great historical interest. It is derived from the leaves of *Lawsonia inermis* or *L. alba*, the ancient gopher-wood of Scripture. It is used for dyeing wool, leather, horse hair, &c., and particularly for staining the nails of the hands and feet an orange-brown colour. The flowers are used in perfumery and embalming, and are also said to possess medicinal properties. It is in common use throughout the East, from Egypt to India.

HESSIAN BLUE (L.) *v.* GENTIAN BLUE 6 B.

HESSIAN BORDEAUX (L.). An azo dye.

Diamidostilbene di-sulphonic acid $\Big\langle$ *Alpha-naphthylamine. Alpha-naphthylamine.*

1886. Greenish crystalline powder, soluble in water with a dark red solution. In concentrated H_2SO_4, blue-violet solution; on dilution, blue-violet ppt.

Application.—A direct cotton colour. Dyes *cotton* claret-red from an alkaline bath.

HESSIAN BRILLIANT PURPLE (L.) (Ber.) (By). An azo dye.

Diamidostilbene di-sulphonic acid $\Big\langle$ *Alpha-naphthylamine sulphonic acid Br. Alpha-naphthylamine sulphonic acid Br.*

1886. Dark red powder, soluble in water. In concentrated H_2SO_4, blue solution; on dilution, blue-black ppt.

Application.—A direct cotton dye. Dyes *cotton* bluish-red from an alkaline bath.

HESSIAN BROWN BB (L.). An azo dye.

Sulphanilic acid Benzidine $\rangle$ Resorcinol. Sulphanilic acid $\rangle$ Resorcinol.

Black brown powder, soluble in water. In concentrated H_2SO_4, violet-black solution; on dilution, brown ppt.

Application.—A direct cotton colour. Dyes *cotton* brown from an alkaline salt bath.

HESSIAN BROWN MM (L.). Similar to the above.

Sulphanilic acid Tolidine $\rangle$ Resorcinol. Sulphanilic acid $\rangle$ Resorcinol.

1889. Brown powder, soluble in water.

Reactions and Application. — Similar to HESSIAN BROWN BB.

HESSIAN PURPLE B (L.) (By.) (Ber.). An azo colour.

Diamidostilbene di-sulphonic acid $\Big\langle$ *Beta-naphthylamine sulphonic acid Br. Beta-naphthylamine sulphonic acid F.*

1886. Brownish powder, giving a cherry-red solution in water. In concentrated H_2SO_4, violet solution; on dilution, brown ppt.

Application.—A direct cotton colour. Dyes *cotton* bluish-red from a soap bath.

HESSIAN PURPLE D (L.) (Ber.) (By.). An azo dye.

Diamidostilbene di-sulphonic acid $\Big\langle$ *Beta-naphthylamine sulphonic acid D. Beta-naphthylamine sulphonic acid D.*

1886. Black powder, giving a yellowish-red solution in water. In concentrated H_2SO_4, violet solution; on dilution, brown solution.

Application.—A direct cotton colour. Dyes *cotton* bluish-red from a soap bath.

HESSIAN PURPLE N (L.) (By.) (Ber.). An azo dye.

Diamidostilbene di-sulphonic acid $\Big\langle$ *Beta-naphthylamine. Beta-naphthylamine.*

1886. Brownish-red powder, soluble in water with a cherry-red colour. In concentrated H_2SO_4, blue solution; on dilution, blue-black ppt.

Application.—A direct cotton colour. Dyes *cotton* bluish-red from a soap bath.

HESSIAN VIOLET (L.) (Ber.) (By.). An azo dye.

Diamidostilbene di-sulphonic acid $\Big\langle$ *Alpha-naphthylamine. Beta-naphthol.*

1886. Black powder, soluble in water with a red-violet solution. In concentrated H_2SO_4, blue solution; on dilution, violet ppt.

Application.—A direct cotton colour. Dyes *cotton* violet from a soap bath.

HESSIAN YELLOW (L.) (Ber.) (By.). An azo dye.

Diamidostilbene di-⟨Salicylic acid.
sulphonic acid   ⟩Salicylic acid.

1886. Ochre-yellow powder, giving a brownish-yellow solution in water. In concentrated H_2SO_4, red-violet solution; on dilution, black ppt.

Application.—A direct cotton colour. Dyes *cotton* yellow from an alkaline bath.

HOECHST NEW BLUE (M.). *New blue* (M.) A rosaniline dye. *Calcium or sodium salt of di- and tri-sulphonic acids of the methyl triphenyl para rosaniline.* 1888. Dark blue powder, soluble in water, but not easily, with a blue colour. In concentrated H_2SO_4, brownish-red solution; on dilution, bright blue solution.

Application.—An acid colour. Dyes *wool* and *silk* in acid bath, bright blue.

HOFMANN'S VIOLETS consist of various *methyl* and *ethyl* derivatives of *para rosaniline* and *rosaniline*. They have now been replaced by the *methyl violets*, with the exception of the red shades.

HOFMANN'S VIOLET. *Red violet 5 R extra* (B.), *Violet 4 R N* (S.C.I.), *Violet 5 R* (Ber.), *Violet R, 2 R* (Mo.). A triphenylmethane dye. Mixtures of *hydrochloride, hydriodide, or acetate of mono-, di-, or tri-ethyl pararosaniline or rosaniline, or the corresponding methyl derivatives.* 1863.

Red Marks.—Green crystalline powders, soluble in water, with a magenta-red colour. In concentrated H_2SO_4, yellow-brown solution; unchanged on dilution.

Violet Marks.—Green glistening powders, giving blue-violet solutions in water. In concentrated H_2SO_4, brownish-yellow solution; on dilution, olive-green, then green, finally blue.

*Application.*—Basic dyes. Dye *wool, silk,* or tannin-mordanted *cotton* red to violet shades.

HOLLYHOCK contains a colouring matter which appears to be identical with, or similar to, indigo, but which is of no importance.

HOMOPHOSPHINE (L.). A bright orange-yellow basic dye.

HYDROCHLORIC ACID, HCl. *Spirits of salt, Muriatic acid.* Hydrogen has a great affinity for chlorine, a mixture of the two gases combining slowly when exposed to diffused daylight, and instantaneously when placed in direct sunlight, or exposed to the flash of burning magnesium, or ignited by an electric spark.

Preparation.—On the large scale hydrochloric acid is produced as a by-product in the manufacture of sodium carbonate by the "Le Blanc process." By this method common salt, NaCl, is decomposed by means of sulphuric acid.

$$2NaCl + H_2SO_4 = 2HCl + Na_2SO_4.$$
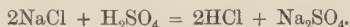
Properties.—Hydrochloric acid is a gas, which combines with water with great avidity. The gas is colourless, and has a very irritating action on the mucous membrane. When the gas is dissolved in water it forms a colourless liquid which fumes in the air. A saturated solution of the gas has a specific gravity of 1·21, and contains 43 per cent. of hydrochloric acid gas. This solution when distilled evolves hydrochloric acid gas, the temperature of the liquid gradually rising to 110° C., when an acid of constant strength distils over. The latter liquid has a specific gravity of 1·101 and contains 20·2 per cent. by weight of HCl. Hydrochloric acid is a very strong acid. It is monobasic and forms salts, termed *chlorides*. The majority of chlorides—*e.g.*, sodium chloride (NaCl)—are soluble in water. Many metals dissolve in hydrochloric acid with evolution of hydrogen. The oxides and hydroxides of most metals are soluble in this acid. Lead is attacked by hot hydrochloric acid, hence leaden pipes and lead-lined tanks cannot be employed in working with the acid. Hydrochloric acid is oxidised by the higher oxides, such as manganese dioxide, lead dioxide, nitric or chromic acid, &c., the hydrogen combining with oxygen to form water, and chlorine being liberated; on this fact depend both the process of producing chlorine from the acid with the aid of manganese dioxide and the energetic action of *aqua regia* (a mixture of nitric and hydrochloric acids).

Commercial hydrochloric acid contains iron, arsenic, sulphuric acid, and organic matter, and has a yellow colour; it is generally pure enough for technical purposes. The commercial product has a specific gravity of 1·12 to 1·19; it is shipped in glass carboys or in large earthenware pots.

The strength of hydrochloric acid is determined by acidimetric titration, or roughly by the hydrometer, the specific gravity increasing with the strength (see following table).

The usual strength of commercial acid is 1·16 specific gravity, which contains 32 per cent. HCl.

The impurities, even in crude acid, being so small in amount, have very little effect upon the density, although, of course, it is possible for the acid to be adulterated with common salt.

Analysis of Hydrochloric Acid.—50 c.c. of the sample are weighed and diluted to 1 litre; 100 c.c. of this solution are titrated with caustic soda, using methyl orange as indicator. 1 c.c. $\frac{N}{1}$ soda = 0·0365 grm. HCl. If sulphuric acid be present it will be necessary

to deduct the acidity due to that acid from the total acidity, after making allowance for any sodium sulphate present.

SPECIFIC GRAVITY OF HYDROCHLORIC ACID AT 15° C., COMPARED WITH WATER AT 4° C. AND REDUCED TO VACUUM. (*Lunge and Marchlewsky.*)

Degrees Twaddell.	Specific Gravity at 15° *in vacuo.*	100 Parts by weight contain Parts by weight of HCl.	1 Litre contains grms. HCl. *
0	1·000	0·16	1·6
1	1·005	1·15	12
2	1·010	2·14	22
3	1·015	3·12	32
4	1·020	4·13	42
5	1·025	5·15	53
6	1·030	6·15	64
7	1·035	7·15	74
8	1·040	8·16	85
9	1·045	9·16	96
10	1·050	10·17	107
11	1·055	11·18	118
12	1·060	12·19	129
13	1·065	13·19	141
14	1·070	14·17	152
15	1·075	15·16	163
16	1·080	16·15	174
17	1·085	17·13	186
18	1·090	18·11	197
19	1·095	19·06	209
20	1·100	20·01	220
21	1·105	20·97	232
22	1·110	21·92	243
23	1·115	22·86	255
24	1·120	23·82	267
25	1·125	24·78	278
26	1·130	25·75	291
27	1·135	26·70	303
28	1·140	27·66	315
29	1·145	28·61	3·8
30	1·150	29·57	340
31	1·155	30·55	353
32	1·160	31·52	366
33	1 165	32·49	379
34	1·170	33·46	392
35	1·175	34·42	404
36	1·180	35·39	418
37	1·185	36·31	430
38	1·190	37·23	443
39	1·195	38·16	456
40	1·200	39·11	469

Sodium chloride is determined by evaporating a weighed portion of the acid to dryness, igniting gently, and testing with $\frac{N}{10}$ silver nitrate (*v.* SODA ASH).

Sodium sulphate may be estimated by evaporating and igniting as in the preceding test, dissolving in water, filtering off insoluble matter, and evaporating to dryness. The residue, which consists of *sodium chloride* and *sodium sulphate*, is weighed. After deducting the amount of sodium chloride

* The number of pounds HCl contained in a gallon is found by dividing the number in the fourth column (grms. HCl per litre) by 100. It will be noticed that each degree Twaddell indicates approximately 1 per cent. HCl.

found as above, the remainder is reckoned as sodium sulphate. The residue should be tested for *lime*, which may be present in small quantities.

Estimation of Hydrochloric Acid. * — Measure off, by means of an accurate pipette, 10 c.c. of the acid, the specific gravity of which should be known, dilute to 200 c.c., take out 10 c.c., and add sodium carbonate, free from chloride, till the reaction is neutral or faintly alkaline. This point will be hit quickly and without the loss of many drops for testing if the percentage of the acid is ascertained from its specific gravity by the table and the corresponding quantity of sodium carbonate solution run in from a burette. Add a little neutral potassium chromate and titrate (*v.* SODIUM CHLORIDE in SODA ASH). The number of c.c. required, multiplied by 73, and divided by the specific gravity of the acid, indicates its percentage of HCl. (This test would fail in presence of metallic chlorides, which, however, seldom occur in appreciable quantity in ordinary hydrochloric acid.)

Sulphuric acid is estimated by nearly neutralising a portion of the diluted acid with sodium carbonate, free from sulphate, and precipitating the sulphuric acid by barium chloride, as mentioned under standard sulphuric acid (*v.* ACIDIMETRY). If the acid be partially neutralised with ammonia, or not neutralised at all, the result is too low. Each part of $BaSO_4$ is equal to 0·34335 SO_3.

Estimation of Iron.—The iron is reduced by digesting the acid for a short time with a rod of zinc free from iron. The rod is well washed, and the whole diluted with water, some manganous chloride or sulphate is added (in order to counteract the action of HCl on permanganate), and the solution titrated with $\frac{N}{50}$ solution of potassium permanganate, each c.c. of which corresponds to 0·00112 grm. Fe.

Arsenic may be determined as in sulphuric acid.

HYDROGEN PEROXIDE, H_2O_2.—Hydrogen peroxide occurs in small quantities in the air and in rain water, having been probably produced by the action of ozone on the moisture contained in the air.

Preparation.—It is prepared artificially by dissolving barium peroxide in acidulated water at a moderate temperature. Other peroxides—*e.g.*, those of sodium or calcium —act in the same way. The reaction proceeds according to the equation—

$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2.$$

The barium peroxide used must be as pure as possible, and in a very finely-divided state. Purity is necessary for a high percentage yield, as the slightest impurity causes the

* Lunge, *The Alkali Makers' Handbook.*

resulting amount of hydrogen peroxide to be lessened. The barium peroxide is soaked repeatedly in water to remove any caustic barium oxide, and eventually passed through a fine sieve, collected on filters and made into a paste. For the preparation of hydrogen peroxide the paste is introduced very slowly into dilute sulphuric acid; care must be taken that the temperature does not exceed 20° C., and the liquid must be stirred continually in order that the peroxide may never remain in contact with neutral parts of the solution; otherwise decomposition takes place immediately, and the yield suffers in consequence. When the solution is nearly neutralised it is advantageous to add sufficient phosphate of soda to replace the free sulphuric acid by phosphoric acid in the free state, since this substance has a preservative influence on the product. The liquid portion is separated from the sediment, the latter washed with water, and the wash waters are run together and made into a 3 per cent. solution, from which the dissolved baryta can be best precipitated by sodium sulphate.

Properties.—Hydrogen peroxide is a colourless odourless liquid. It has been concentrated *in vacuo* to a syrup of $1 \cdot 45$ specific gravity, which does not solidify at $-30°$ C. It possesses a bitter, astringent taste, mixes with water in all proportions, and evaporates *in vacuo.* Very diluted aqueous solutions can be boiled without the peroxide being decomposed, a part of it escaping together with the steam.

The peroxide is very unstable in concentrated solutions, and decomposes readily with evolution of oxygen; in diluted and slightly acidulated solutions it keeps better. The decomposition takes place even at a medium temperature, and by heating it can be increased to an explosion. In consequence of this easy decomposition, and owing to the fact that oxygen is given off in the nascent state, hydrogen peroxide acts as a powerful oxidising agent. Thus chromic oxide (Cr_2O_3) and arsenic (the element) are converted into chromic and arsenic acids respectively, sulphides are transformed into sulphates (*e.g.,* PbS into $PbSO_4$); organic colouring matters are decolorised and destroyed; from sulphuretted hydrogen, sulphur, and from hydrochloric and hydriodic acids, chlorine and iodine respectively are separated; for example—

$$H_2O_2 + 2HI = I_2 + 2H_2O.$$
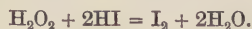
An addition of 2 per cent. of alcohol or ether is effectual in retarding the decomposition of hydrogen peroxide solutions.

R. Wolffenstein * states that under certain conditions peroxide of hydrogen is not nearly

so susceptible to the action of heat as is generally supposed to be the case.

If the following substances :—

(1) All compounds showing an alkaline reaction,

(2) Compounds of the heavy metals (even traces),

(3) All solid substances, even such as are chemically indifferent,

are absent, hydrogen peroxide is little affected by heat, and can be concentrated and distilled to any desired extent.

The impurities sometimes found in the commercial product are hydrochloric, phosphoric, and sulphuric acids, and their salts, and small quantities of lime, magnesia, alumina, potash, and soda, and occasionally lead, iron, copper, and manganese.

If an aqueous solution of hydrogen peroxide be shaken with ether, the latter substance dissolves out the peroxide of hydrogen forming a stable solution which can be distilled without decomposition.

Hydrogen peroxide acts slowly on a solution of pure potassium iodide; but iodine is separated immediately on addition of ferrous sulphate (and can be recognised by the reaction on starch paste). The oxides of barium, magnesium, and zinc are oxidised by peroxide of hydrogen into the peroxides; for instance—

$$MgO + H_2O_2 = MgO_2 + H_2O.$$

H. Koechlin makes use of this fact in the bleaching of cotton.*

In the above cases hydrogen peroxide is an oxidising agent, but some substances, such as unstable oxides, are reduced by it; for example, the oxides of mercury, silver, and gold, and certain acids such as chromic and permanganic acids.

Chlorine in aqueous solution is oxidised to hypochlorous acid and subsequently reduced to hydrochloric acid :—

1. $Cl_2 + H_2O_2 = 2HOCl.$
2. $HOCl + H_2O_2 = HCl + H_2O + O_2.$

Hydrogen peroxide is also resolved into water and oxygen by many substances in a finely-divided state—*e.g.,* gold, platinum, silver, carbon, or manganese peroxide.

Commercial peroxide of hydrogen forms a colourless liquid which contains about 3 per cent. H_2O_2 in aqueous solution. The strength of the commercial article is expressed in *volumes* of *available oxygen.*

Hydrogen peroxide may be stored in well-tarred casks, in *bright* tin vessels, or in such as have been coated with amber varnish, or in glass vessels. Since many metals have a catalytic action on the substance, decomposing it into water and oxygen, it is generally

---

* *Journ. Soc. Dyers and Col.,* 1895, p. 22.

* Prudhomme, *Journ. Soc. Dyers and Col.,* 1891, p. 136.

used in earthenware or wooden vessels. It should not be exposed to light or heat, and should not be stored in tightly closed vessels, else these might be broken by inside pressure from evolved oxygen.

Hydrogen peroxide is the best bleaching agent known for all classes of fibres. Owing to its high price its application was restricted for some time to the bleaching of tussur-silk and feathers, but it is now used in increasing quantities for the bleaching of woollen goods.

Peroxide of hydrogen solution is usually sold containing ten, twelve, or fifteen volumes of oxygen. This denotes that one volume of the liquid contains peroxide in such quantity as to evolve ten, twelve, or fifteen volumes of oxygen respectively when reduced to water. The *value* of a sample depends upon the amount of *available oxygen* present.

Analysis—Estimation by Iodine and Thiosulphate.—Kingzett[*] has shown that the best method of estimating peroxide of hydrogen is by means of iodine and thiosulphate. The peroxide in an acid solution liberates an equivalent of iodine from potassium iodide, which is then estimated by $\frac{N}{10}$ thiosulphate. About 10 c.c. of the sample are mixed with 30 c.c. of a mixture of equal volumes of water and sulphuric acid, and an excess of potassium iodide added. After standing about five minutes, the liberated iodine is titrated with $\frac{N}{10}$ thiosulphate and starch, as described under chloride of lime (*v.* Calcium Chloro-hypochlorite).

1 c.c. of $\frac{N}{10}$ thiosulphate = 0·0017 grm. of H_2O_2 or 0·0008 grm. of O_2.

1 grm. oxygen = 697·5 c.c. at 0° C.

Estimation by Potassium Permanganate.— In the absence of other bodies acted upon by permanganate, this forms a ready means of determining the value of hydrogen peroxide. A measured quantity of the sample is acidulated with sulphuric acid, and $\frac{N}{10}$ permanganate added until a faint pink colour appears. This method is based on the following reaction :—

$$5H_2O_2 + 2KMnO_4 + 3H_2SO_4 =$$
$$2MnSO_4 + K_2SO_4 + 8H_2O + 5O_2.$$
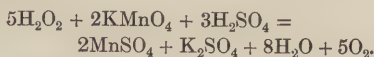
1 c.c. of $\frac{N}{10}$ permanganate = 0·0017 grm. of H_2O_2.

Gasometric Determination. — Coulamine[†] recommends the following process as a rapid means of estimating hydrogen peroxide :— 10 to 20 c.c. are neutralised with ammonia and diluted to 250 c.c. 25 c.c. of this solution are introduced into a gas absorption tube graduated for 50 c.c. in $\frac{1}{10}$ c.c., a few crystals of potassium permanganate wrapped

* *Journ. Chem. Soc.* (Tr.), 1880, p. 792.
† *Journ. Soc. Dyers and Col.*, 1886, p. 7.

in tissue paper are added, the tube quickly closed by the thumb and vigorously shaken. When the reaction is complete, the tube is inverted over water and raised or lowered until the liquid in both vessels is at the same level. The volume of the evolved gas is then read off.

This method, however, is not very exact.

Qualitative Reactions.—A solution of guaiacum, together with a small quantity of blood, gives a blue coloration in the presence of hydrogen peroxide.

When a solution of bichromate of potash and hydrochloric acid is agitated with hydrogen peroxide and ether, the etherial layer assumes a blue colour.

HYDROMETER and Specific Gravity. The concentration of a liquid such as sulphuric acid, or the amount of solid substance present in such a solution as "nitrate of iron" may frequently be measured by a determination of the *density* or *specific gravity* of the liquid. This is most accurately done by weighing a known volume of the liquid, since the specific gravity of any substance is represented by the weight of that substance compared with the weight of an equal volume of water, the latter being taken as unity.

Thus—

50 c.c. of water weigh 50 grms.

50 ,, of sulphuric acid weigh 92 grms. ; therefore the weight of sulphuric acid compared with water is as 92 : 50, and the specific gravity $= \frac{92}{50} = 1·84$.

The determination of specific gravity by this method necessitates the use of accurately gauged instruments, and requires considerable time and a certain degree of manipulative skill. For use in a works a simpler and more expeditious process is desirable, and such is found in the use of the instruments known as *hydrometers* or *aereometers*, which, by simple immersion in the liquid, show on a scale the approximate specific gravity.

The instrument depends for its action upon the obvious fact that the heavier a liquid is the heavier the float which it will support. It takes the form of weighted bulbs supporting upright graduated scales, a series of such instruments being so weighted that the stem of No. 2 is almost entirely *immersed* in a liquid which floats No. 1—which is lighter—so high that the stem is nearly all *above* the liquid. One set of instruments, usually six in number, thus constitutes a complete scale of wide range.

The method of graduating the scale varies in different instruments. Some are arranged to indicate directly the actual specific gravity, and are known as *specific gravity hydrometers*, but those most commonly in use in England, and which are known as *Twaddell's hydro-*

meter, are graduated with an empirical scale, which, however, bears a definite ratio to specific gravity. Another scale, largely used on the Continent of Europe and in America, is known as *Baumé's*, and this cannot be converted into specific gravity without the aid of a complicated formula or reference to a table.

A revised Baumé scale is now in limited use; and this, which is known as the *rational Baumé* scale, is directly convertible into specific gravity by a simple formula.

Other scales have been proposed and are met with occasionally, such as those of *Beck, Cartier, Balling*, and *Gay Lussac*. All these bear a definite relationship to specific gravity, and a table is attached by means of which any particular scale may be converted into specific gravity, or, indirectly, into another more convenient scale.

HYDROMETER SCALE.	FORMULA for Converting into *Specific Gravity* (Sp. gr.).
Specific gravity hydrometer.	Gives direct readings.
Twaddell's hydrometer.	$Sp.\ gr. = \dfrac{0\cdot5\ N + 100}{100}$
Rational Baumé.	$Sp.\ gr. = \dfrac{146\cdot3}{146\cdot3 - N}$
Beck's hydrometer.	$Sp.\ gr. = \dfrac{170}{170 - N}$
Cartier's hydrometer.	$Sp.\ gr. = \dfrac{136\cdot8}{136\cdot8 - N}$
Balling's hydrometer.	$Sp.\ gr. = \dfrac{200}{200 - N}$
Gay Lussac's hydrometer.	$Sp.\ gr. = \dfrac{100}{100 - N}$

In the above formulæ N = the particular degree which it is desired to convert; thus if it is desired to change 168° Twaddell into specific gravity,

$$\frac{(168 \times 0\cdot5) + 100}{100} = 1\cdot84\ sp.\ gr.$$

In determining the specific gravity of a liquid two facts must be kept in view—viz., that the presence of a second substance in solution entirely vitiates any inference which may be drawn with regard to the amount of the principal substance present; and secondly, that the specific gravity is greatly influenced by the temperature at which the experiment is made. Thus, if a sample of "nitrate of iron" is adulterated with sodium sulphate, it may show a high specific gravity and yet be weak in iron; or again, to illustrate the effect of temperature, aniline oil will sink in cold water, because it is heavier at low tem-

peratures, but if the mixture is heated the oil will rise to the surface and float, because as it expands more quickly than water it becomes lighter at the higher temperature.

The determination of specific gravity should therefore always be made at as near 15° C. (60° F.) as possible, this being taken as the *standard temperature* for such determinations.

The annexed table gives a comparison between specific gravity and degrees Twaddell and Baumé:—

Tw.	B.	Sp. Gr.	Tw.	B.	Sp. Gr.
degs.	degs.		degs.	degs.	
1	0·7	1·005	88	44·1	1·440
2	1·4	1·010	89	44·4	1·445
3	2·1	1·015	90	44·8	1·450
4	2·7	1·020	91	45·1	1·455
5	3·4	1·025	92	45·4	1·460
6	4·1	1·030	93	45·8	1·465
7	4·7	1·035	94	46·1	1·470
8	5·4	1·040	95	46·4	1·475
9	6·0	1·045	96	46·8	1·480
10	6·7	1·050	97	47·1	1·485
11	7·4	1·055	98	47·4	1·490
12	8·0	1·060	99	47·8	1·495
13	8·7	1·065	100	48·1	1·500
14	9·4	1·070	101	48·4	1·505
15	10·0	1·075	102	48·7	1·510
16	10·6	1·080	103	49·0	1·515
17	11·2	1·085	104	49·4	1·520
18	11·9	1·090	105	49·7	1·525
19	12·4	1·095	106	50·0	1·530
20	13·0	1·100	107	50·3	1·535
21	13·6	1·105	108	50·6	1·540
22	14·2	1·110	109	50·9	1·545
23	14·9	1·115	110	51·2	1·550
24	15·4	1·120	111	51·5	1·555
25	16·0	1·125	112	51·8	1·560
26	16·5	1·130	113	52·1	1·565
27	17·1	1·135	114	52·4	1·570
28	17·7	1·140	115	52·7	1·575
29	18·3	1·145	116	53·0	1·580
30	18·8	1·150	117	53·3	1·585
31	19·3	1·155	118	53·6	1·590
32	19·8	1·160	119	53·9	1·595
33	20·3	1·165	120	54·1	1·600
34	20·9	1·170	121	54·4	1·605
35	21·4	1·175	122	54·7	1·610
36	22·0	1·180	123	55·0	1·615
37	22·5	1·185	124	55·2	1·620
38	23·0	1·190	125	55·5	1·625
39	23·5	1·195	126	55·8	1·630
40	24·0	1·200	127	56·0	1·635
41	24·5	1·205	128	56·3	1·640
42	25·0	1·210	129	56·6	1·645
43	25·5	1 215	130	56·9	1·650
44	26·0	1·220	131	57·1	1·655
45	26·4	1·225	132	57·4	1·660
46	26·9	1·230	133	57·7	1·665
47	27·4	1·235	134	57·9	1·670
48	27·9	1·240	135	58·2	1·675
49	28·4	1 245	136	58·4	1·680
50	28·8	1·250	137	58·7	1·685
51	29·3	1·255	138	58·9	1·690
52	29·7	1·260	139	59·2	1·695
53	30 2	1·265	140	59·5	1·700
54	30·6	1·270	141	59·7	1·705
55	31·1	1·275	142	60 0	1·710
56	31·5	1·280	143	60·2	1·715
57	32·0	1·285	144	60·4	1·720
58	32·4	1·290	145	60·6	1·725
59	32·8	1·295	146	60·9	1·730
60	33·3	1·300	147	61·1	1·735

Tw.	B.	Sp. Gr.	Tw.	B.	Sp. Gr.
degs.	degs.		degs.	degs.	
61	33·7	1·305	148	61·4	1·740
62	34·2	1·310	149	61·6	1·745
63	34·6	1·315	150	61·8	1·750
64	35·0	1·320	151	62·1	1·755
65	35·4	1·325	152	62·3	1·760
66	35·8	1·330	153	62·5	1·765
67	36·2	1·335	154	62·8	1·770
68	36·6	1·340	155	63·0	1·775
69	37·0	1·345	156	63·2	1·780
70	37·4	1·350	157	63·5	1·785
71	37·8	1·355	158	63·7	1·790
72	38·2	1·360	159	64·0	1·795
73	38·6	1·365	160	64·2	1·800
74	39·0	1·370	161	64·4	1·805
75	39·4	1·375	162	64·6	1·810
76	39·8	1·380	163	64·8	1·815
77	40·1	1·385	164	65·0	1·820
78	40·5	1·390	165	65·2	1·825
79	40·8	1·390	166	65·5	1·830
80	41·2	1·400	167	65·7	1·835
81	41·6	1·405	168	65·9	1·840
82	42·0	1·410	169	66·1	1·845
83	42·3	1·415	170	66·3	1·850
84	42·7	1·420	171	66·5	1·855
85	43·1	1·425	172	66·7	1·860
86	43·4	1·430	173	67·0	1·865
87	43·8	1·435			

I

IMMEDIAL BLACK (C.). 1898. *Immedial black V extra and G extra.* 1899. Sulphide colours, identical with, or very similar to, *Vidal black* (*q.v.*). *v.* also SULPHIDE COLOURS.

IMMEDIAL BLUE C (C.). 1899. A sulphide colour allied to *Immedial black*, and producing very fast navy-blues by a similar process. *v.* SULPHIDE COLOURS.

IMPERIAL GREEN *v.* MALACHITE GREEN.

IMPERIAL RED *v.* BENZOPURPURIN 4 B.

IMPERIAL SCARLET (By.) *v.* PONCEAU 3 R B.

IMPERIAL YELLOW *v.* AURANTIA.

INDAMINE 3 R (N.J.). *Benzindamine.* Constitution unknown. Obtained by the action of *nitrosodimethylaniline hydrochloride* upon *ortho-toluidine hydrochloride.* 1889. Blackish powder, giving a red-violet solution in water. In concentrated H_2SO_4, green solution; on dilution, first blue, then red.

Application.—A basic colour. Dyes tannin-mordanted *cotton* bluish-violet.

INDAMINE 6 R (N.J.). Obtained as above, but from a mixture of *ortho-* and *para-toluidine.* 1889.

Appearance, Reactions, and Application.— Similar to INDAMINE 3 R.

INDAZINE M (C.). An azine derivative. *Dimethylphenylsafranine chloride.* 1888. Bronzy powder, slightly soluble in water, with a blue colour. In concentrated H_2SO_4, blackish-green solution, becoming blue on dilution.

Application.—A basic colour. Dyes tannin-mordanted *cotton* blue.

INDAZURIN (Bind.). A basic dye, producing navy-blue shades on tannin-mordanted *cotton.*

INDIAN YELLOW or **PUVREE.** Is a yellow colouring matter of disputed origin. It is imported from India and China, and is used mainly as an artist's pigment. When boiled with a solution of borax it dissolves, and this solution produces a bright yellow colour on *silk* or *cotton* mordanted with alumina.

INDIAN YELLOW (By.) *v.* AZO YELLOW.

INDIAN YELLOW C (C.) *v.* AZO YELLOW.

INDIGEN D and F (By.) *v.* INDULINE.

INDIGO.—Indigo has long been regarded as one of the most valuable and important of all colouring matters. It was used in India and Egypt long before the Christian era, and it has been proved that blue ribbons found on Egyptian mummies 5000 years old had been dyed with indigo. It was introduced into Europe in the sixteenth century, but for a great many years very little was used on account of the opposition of the woad cultivators, who induced the English, French, and German Governments to prohibit its use. The cultivators of woad contended that indigo was not only a fugitive dye, but that it was a "corrosive and pernicious drug." In reality they feared that the importation of indigo would ruin their trade in woad. In France the law was so severe that Henry IV. issued an edict condemning to death any one who used that "pernicious drug," which was called the "devil's food."

The indigo plant thrives only in tropical climates, and by far the greatest amount of indigo is obtained from India, and more especially from Bengal, Oude, and Madras. It is also manufactured in Java, Manilla, China, Japan, Central America, Brazil, and certain parts of Africa. The principal plants cultivated for the manufacture of this dye are the *Indigofera tinctoria, Indigofera anil, Indigofera disperma,* and *Indigofera argentea.* There are numerous other varieties of lesser importance.

Indigo is also obtained from other plants besides those belonging to the genus *Indigofera,* but to a comparatively small extent. Among these may be mentioned *Wrightia tinctoria* (cultivated to some extent in Madras), *Strobilanthes flaccidifolius* (Assam), *Tephrosia toxicaria* (Bombay and Rajputana), *Polygonum tinctorium* (China and Russia), *Zonchocarpus cyanesceus* (West Coast of Africa), *Isatis tinctoria* (China, Afghanistan, &c.). The *Isatis tinctoria* or woad-plant was formerly largely cultivated in Europe, and was used exclusively up to the sixteenth century. It is still grown in Lincolnshire

and on the Continent (South of France, Hungary, &c.), but is now never used alone for dyeing. It is employed in the fermentation vats in dyeing woollen goods. These vats are thus in consequence termed *woad-vats*. The woad assists the fermentation, and dyers further contend that it causes the indigo to penetrate more thoroughly into the interior of the fibre.

An interesting account of the cultivation and manufacture of woad as carried out at the present day is given in *Nature*,[*] by Darwin and Meldola.

The cultivation and manufacture of indigo in Northern Bengal have been described by Rawson in the *Journ. Soc. Chem. Industry*,[†] and the *Journ. Soc. Dyers and Colourists*.[‡]

CULTIVATION.—As already mentioned, a great many plants are capable of yielding indigo, but *Indigofera tinctoria* is the only one cultivated in Bengal. Previous to sowing the seed, the land undergoes a rather elaborate process of preparation. In October, soon after the manufacturing season or "Mahai" is at an end, the land is dug by means of a large hoe. After hoeing, the land is ploughed. Usually about half-a-dozen bullock-drawn ploughs are driven close together from end to end of a field, whilst across the furrows thus made another half-dozen work at right angles. After ploughing, a pole five to eight feet in length with one side flat is drawn across the land. This implement, drawn by two to four bullocks, is called a "hanga." The flat side is on the ground, a driver stands at each end, and the "hanga" is dragged backwards and forwards over the land. This has the effect of breaking the clods and smoothing the land. Sometimes a heavy roller is also used, but only where clods will not give way to the "hanga." The land is then ploughed again three or four times. Finally, the small clods of earth are pulverised by women and children, who use short thick sticks for the purpose. They also collect and remove all loose rubbish, such as grass, weeds, and stumps of the previous season's crop. The seed is sown by drills about the end of February or beginning of March. It germinates in the course of four or five days, and by the middle of June, when the manufacturing season usually commences, the plant has obtained a height of from three to five feet, and has a stem of about a quarter of an inch in diameter.

The above is a description of the methods generally followed, but in several large concerns steam cultivation has been introduced, and the most modern agricultural machinery has been for some time in use.

The indigo crop is a very precarious one ; too much or too little rain is equally destructive. After a few weeks' growth the plant may appear to be flourishing beautifully, when the tap root going deeper into the ground comes across a dry layer of soil ; the plant then rapidly withers and dies, and the planter has to begin his sowings over again. Rain falling in February or March on seed recently sown or on plants just through the soil will also necessitate re-sowing. In bad seasons this re-sowing may have to be done three or four times. The leaf of the plant is of a yellowish-green colour, and shows no indication whatever of its containing anything productive of a blue colouring matter.

The following table (A) shows the mean results of twelve samples as analysed (air-dried), and also calculated on the green plant containing (as it does on an average) 75 per cent. of water. The upper part of A gives the total nitrogenous and mineral matters (ash), and the lower portion, to which cross references are made, the proportion of nitrogen and the composition of the ash. The composition of the mineral matter in 100 parts is shown in Table B.

A.—ANALYSIS OF INDIGO PLANT

(*Indigofera tinctoria*).

	Air-dried.		Green Plant.	
	Leaves.	Stems.	Leaves.	Stems.
Water, ...	10·42	9·75	75·00	75·00
*Nitrogenous matters,	29·37	5·94	8·19	1·65
Oil, &c., soluble in ether, ...	3·85	1·05	1·07	·29
Woody fibre, ...	11·07	47·50	3·09	13·16
Carbo-hydrates and other organic matter, ...	33·29	31·01	9·30	8·60
†Mineral matter (ash),	12·00	4·75	3·35	1·30
	100·00	100·00	100·00	100·00
Matter soluble in water—				
Organic, ...	25·05	9·05	6·99	2·51
Mineral, ...	7·55	2·65	2·11	·73
*Containing nitrogen,	4·64	·94	1·293	·260
†Mineral matter containing—				
Silica, ...	·628	·051	·175	·013
Phosphoric acid, .	·916	·344	·255	·095
Sulphuric acid, . .	·296	·074	·084	·021
Carbonic acid, &c., .	2·885	1·163	·806	·323
Chlorine, ...	·050	·074	·014	·021
Oxide of iron and alumina, ...	·086	·020	·024	·006
Oxide of manganese,	·040	·025	·011	·008
Lime, ...	3·591	1·275	1·002	·353
Magnesia, . . . ¿ .	1·298	·164	·362	·045
Potash, ...	2·210	1·460	·616	·404

B.—Composition of Ash in 100 parts.

	Leaves.	Stems.
Silica,	5·23	1·10
Phosphoric acid,	7·64	7·40
Sulphuric acid,	2·46	1·58
Carbonic acid, &c.,	24·05	25·03
Chlorine,	·41	1·58
Oxide of iron and alumina,	·71	·43
Oxide of manganese,	·33	·53
Lime,	29·94	27·43
Magnesia,	10·82	3·50
Potash,	18·41	31·42
	100·00	100·00

The different samples showed a considerable variation in their composition. The mineral matter varied in the air-dried leaf from 8·40 per cent. to 14·40 per cent. One sample contained 5·48 per cent. of nitrogen, whilst another showed only 3·75 per cent. As shown by the "carbolic acid method" about four-fifths of the total nitrogen present in leaves exist in the form of albuminoid compounds.

The proportion of leaf and stem in the indigo plant varies greatly. The mean result of twenty determinations gave, in round numbers, 40 per cent. of leaf and 60 per cent. of stem. On this basis, the composition of the whole green plant will be as follows :—

C.—Showing Composition of whole Green Plant.

Water,	75·00
*Nitrogenous matters,	4·27
Oil, &c., soluble in ether,	·60
Woody fibre,	9·14
Carbo-hydrates and other organic matter,	8·87
+Mineral matter (ash),	2·12
	100·00
Matter soluble in water—	
Organic,	4·30
Mineral,	1·28
*Containing nitrogen,	·673
+Mineral matter containing—	
Silica,	·078
Phosphoric acid,	·159
Sulphuric acid,	·046
Carbonic acid, &c.,	·519
Chlorine,	·018
Oxide of iron and alumina,	·013
Oxide of Manganese,	·009
Lime,	·615
Magnesia,	·172
Potash,	·491

There is a very great variation in the amount of plant yielded by an acre of land. A fair average crop may be taken at 50 to 60 cwts. per acre. Taking the lower figure, a crop of indigo plant removes 118 lbs. of mineral matter from an acre of land. Of this amount 9 lbs. are phosphoric acid and 27½ lbs. potash. The plant from an acre of land also contains 37·7 lbs. of nitrogen, but as indigo is a *legu-minous* plant, a portion of this nitrogen is probably derived from the atmosphere. With a few trifling exceptions, the only manure used for the cultivation of the indigo plant is the residue of the plant itself after the colouring principles have been extracted. The refuse plant, which is called "seet," is usually only applied to land near the factories, so that much of the land has been growing indigo for years without the application of any fertilisers. The refuse plant is a valuable manure. It contains practically all that is necessary for the growth of a new crop. The air-dried "seet" contains a greater percentage of nitrogen than the original plant (air-dried), and the ash contains more phosphoric acid, though rather less potash, than the ash of the original plant.

The soils of Behar contain an abundance of potash and a fair proportion of phosphoric acid. As a rule they contain but a small proportion of nitrogen. This is rather remarkable in consideration of the large percentage of nitrogen present in the plant, but, as already stated, a portion of this element is no doubt derived from the atmosphere. Dr. Voelcker in his report on "Indian Agriculture," 1893, and Dr. Leather in the *Agricultural Ledger*, 1898, call attention to the small percentage of nitrogen to be found in Indian soils generally.

The following table contains the results of analyses of four samples of indigo soils from Behar :—

D.—Composition of Bengal Indigo Soils.

In 100 parts of Dry Soil	Champarun District.		Tirhoot District.	
	Light Sandy.	Heavy Clay.	A.	B.
*Organic matter and combined water,	1·40	1·95	2·60	2·55
Sand and insoluble silicates,	53·85	87·55	87·90	88·85
Phosphoric acid (P_2O_5),	·17	·13	·10	·12
Sulphuric acid (SO_3),	·05	·04	·03	·02
Carbonic acid, &c. (by diff.),	17·37	1·06	·67	1·01
Oxide of iron,	2·25	3·90	2·60	2·90
Alumina,	3·75	4·20	3·35	3·65
Lime,	20·60	·42	1·05	·40
Magnesia,	·22	·45	1·30	·16
Potash,	·34	·30	·40	·34
	100·00	100·00	100·00	100·00
*Containing nitrogen,	·065	·055	·080	·065
Equal to ammonia,	·078	·066	·097	·078

A great many of the soils contain about 20 per cent. of lime, whilst a number of others (heavy clay soils) contain 0·5 to 1 per cent. only.

MANUFACTURE.—The manufacture of indigo in Behar is carried out almost entirely under the direction of Europeans. The manufacturing season usually commences about the middle of June, but it may be a fortnight earlier or a fortnight later. Soon after cutting, the plant throws forth fresh leaf, and after two or three months a second crop is obtained. The first and principal crop is called the "Morhan" crop, and the second the "Khoonties." The manufacturing seasons are spoken of as the "Morhan Mahai" and the "Khoontie Mahai" respectively. In some cases a week or a fortnight elapses between the two seasons, in others there is no break. The plant is cut early in the morning, often before daybreak, and taken to the factory in carts, each drawn by two bullocks. The work on an indigo "concern" is usually divided among a number of factories —from two to ten or twelve, according to the size of the concern. Each factory deals with plant grown within a radius of four or five miles. At a moderate-sized factory some hundreds of cart loads of plant are treated every day throughout the manufacturing season. The scene presented in the morning round the steeping vats, with the long lines of heavily laden bullock carts slowly wending their way from various points towards the factory, is a very busy and imposing one.

The principal part of an indigo factory consists of steeping vats and beating vats. The former are arranged on a higher level than the latter. Each steeping vat has a capacity of a little over 1000 cubic feet. The actual dimensions are 18 ft. by 16 ft. by 3 ft. 9 in. in depth. The depth being measured to the cross beams and not to the top of the vat. Each range of beating vats runs the whole length of the steeping vats and has a width of 13 ft. 6 in. ; a wall 3 ft. high runs down the centre of the beating vat, but a space is left at each end so as to allow of a free circulation of the liquid when the wheel is set in motion. The beating wheel consists of a shaft armed with three sets of spokes. These spokes (six in number in each set) are furnished at the extremities with blades which, in revolving, churn up the liquid and cause a continual circulation. In some cases the steeping vat is divided into three parts, and the wheel works in the central division. The vats are built of brickwork faced with Portland cement. They are usually open to the air, though in some cases the steeping vats are covered. There are great variations in the arrangements of vats in different factories. In some cases there are as many as eight steeping vats to one beating vat. The steeping vats are frequently arranged on each side of two or three ranges of beating vats, whilst in other cases the steeping vats are arranged in long rows with the beating vats alongside at a lower level. Formerly the steeping vats were much larger than at present, having a capacity of about 2000 cubic feet, and each vat had a corresponding beating vat. The liquid was "beaten" by hand instead of by the wheel, and each vat required twelve coolies armed with beating sticks. In Madras and the North-West Provinces this method is still generally followed, and some factories in Behar have also a few hand-beating vats. In addition to the vats the requisite plant of an indigo factory includes a steam boiler and engine, pumps, boiling tanks, draining tables, presses, drying-house, and various workshops. On a higher level than the steeping vats a large water tank or "kajana" is situated. This is sometimes made of iron, but more usually it is constructed of brickwork and Portland cement, like the vats. The water is pumped into the "kajana" from the neighbouring river, stream, or lake, and from it the steeping vats are filled.

Loading the Vats in Steeping.—In the first place the vats are thoroughly cleansed ; this is carefully done every day. A number of coolies enter the vat and scrub every part well, using a plentiful supply of water. The plant is then closely stacked in the vat in a more or less upright position, so as to allow the entangled air to escape more freely and the liquid, after steeping, to drain away more completely.

The amount of green plant put into a vat of 1000 cubic feet capacity varies from 11,000 to 15,000 lbs. When filled, a number of pieces of bamboo are placed across the top and the whole kept in position by three or four stout pieces of timber fixed by iron pins running through racks attached to the sides of the vat. (Bridges-Lee, in his book on *Indigo Manufacture*, recommends a dead weight to keep the plant immersed.) Water is now run into the vat until it reaches within a few inches of the beams. If filled completely, the liquid would subsequently overflow, as the plant undergoes a considerable expansion during the steeping process. A great pressure is thus exerted, and occasionally a beam is broken or the vat gives way. The length of time required for extracting the colour-yielding principles varies from nine to fourteen hours, according to the temperature and other climatic conditions. Ten to eleven hours may be considered a fair average period. The temperature of the water in June, July, and part of August is usually from 88° to 95° F., whereas in September it falls to about 80°, when a longer steeping is necessary. Indigo plant is not easily wetted by water, and for an hour or two no action takes place. As pointed out by Bridges-Lee, the leaves of the plant are covered by an immense number of small

hairs, which no doubt are the chief cause of their water-repelling property, which, however, is also due to the vitality of the plant itself. When once the water comes into intimate contact with the leaf the colouring principle is readily extracted, being very soluble in water. After two or three hours the liquid rises in the vat, bubbles of air are liberated, and the surface becomes covered with a thick froth. Carbon dioxide is evolved in large quantities, and, in the later stages, either marsh gas or hydrogen, or a mixture of the two, is freely given off. If a light be applied to the surface of the vat towards the end of the steeping operation a blue flame extending for several yards may frequently be obtained. The vat has certainly the appearance of being in a state of active fermentation. After a time the liquid subsides, and this is the chief indication to the overseer, or the manager, that the plant is sufficiently steeped. The valve is now opened and the liquid run into the beating vat. In many cases a large wooden plug is used instead of a valve.

After the solution has run off, the plant is, of course, saturated with the same liquid, and even if all the colouring principle is extracted from the leaf it would appear that a second steeping or at least a washing would be advantageous. The leaf, which prior to steeping was of a yellowish colour, is now bluish-green, and *appears* to be much more capable of yielding indigo than the original plant. It has been found in practice, however, that a second steeping is unprofitable. Certain chemical and bacteriological changes take place much more rapidly on wet matter offering a great surface than when the same material is either dry or completely immersed in water. Whilst the liquid is draining off from the plant, it would seem that the colour-giving principle, which is left in solution on the leaves and twigs, is rapidly decomposed and destroyed. A small portion forms indigo blue, but this is left on the plant in an insoluble state, and is, therefore, not extracted by a second steeping. After the water has run off, the temperature of the plant rises rapidly.

The extracted plant or "seet" is taken out to be subsequently applied as manure to the land, and the vats prepared for another steeping.

Beating.—The liquid running from the steeping into the beating vat varies in colour from a bright orange to an olive green, and possesses a peculiar fluorescence. When sufficiently steeped, the liquid which runs out at first is of an orange colour, but it soon changes to a yellow and finally to an olive. When all the vats are discharged, the wheel is set in motion, at first slowly and gradually increased to a maximum. Under normal conditions from two to three hours are required to complete the operation of beating; although in some cases the length of time may be reduced to one or one and a-half hours. A considerable amount of froth is formed, especially if the plant has been oversteeped. In such cases there is frequently a froth of two or three feet in depth on the surface of the liquid. This is kept down as much as possible by coolies, who walk through the liquid with a cloth stretched across the vat and bring the froth under the beating wheel, where much of it is broken up. When nearing completion the froth, which at first was bluish, becomes white and gradually disappears. In the meantime, the liquid changes through various shades of green to a deep indigo blue. In order to ascertain when the beating is complete, the foreman or "mal mistri" takes up some of the liquid and pours it on to a white plate. If the grain or "fecula" readily settles, leaving a clear fluid, the beating is considered accomplished and the wheel is stopped. Sometimes a little lime is added to the contents of the plate. A better plan is to saturate a piece of filter paper with the solution and subject it to the fumes of ammonia. If the slightest blue coloration is developed, it is an indication that the beating is not complete. In place of the beating wheel, various other devices for oxidising the liquid have been tried, but not generally adopted. The most promising alternative methods appear to be drawing air through the liquid by means of a steam "blower" or a shower bath arrangement devised by Bridges Lee.

After beating, the indigo "fecula" is allowed to settle, which usually takes two or three hours, when the supernatant liquid "seet water" is run off either by means of a surface drainer or by removing a series of wooden plugs arranged down the side of the vat. The bottom of the vat is inclined towards one corner where the precipitated indigo or "mal" is collected, passed through one or two strainers, whence it flows to a well or "mal jhari," from which it is elevated, usually by means of a steam injector, to a large rectangular iron tank. The "mal" is strained again twice on its way from the well to the boiling tank. Every precaution is taken to keep the indigo clean and free from bits of twigs and dirt.

Boiling and Filtering.—The liquid containing indigo in suspension (to the extent of about 0·5 per cent.) when lifted by the steam injector has usually a temperature of 140° to 150° F. It is not always actually boiled, but is heated (now usually by steam, but in some cases by direct fire, or by steam and direct fire combined) up to temperatures varying from 190° to 212° F. In some cases the steam is shut off as soon as the liquid begins to boil;

in others, the boiling is continued for a quarter or half an hour. There is a three-fold object in boiling the "mal"; 1st, it prevents putrefaction, which rapidly takes place in such a hot moist climate as that of India during the manufacturing season, and would result in much loss of colour; 2nd, it dissolves some of the brown matters which have precipitated with the indigo fecula and thus produces a finer quality; 3rd, it causes the indigo particles to settle more readily, so that the refuse liquor may be run off without delay. In some factories the supernatant liquid is run off from the boiler, fresh water added, and the whole boiled up a second time. After boiling, the indigo is allowed to settle, the clear liquid is run off as far as possible, and then the hot concentrated "mal" is run through strainers on to a large filter known as the "table" or "dripping vat." This is constructed of narrow parallel laths fixed close together on a stout wooden frame with sides about 18 ins. high sloping outwards. The "table," which stands in a shallow trough made of cement, is covered with a sheet of strong cloth specially made for the purpose. At first the liquid comes through blue and cloudy, and it is pumped back on to the cloth until it is perfectly clear. It is then usually of a sherry colour. Much of the liquid passes through the filter cloth, but a considerable portion is also removed by carefully letting down a corner of the cloth after the precipitate has settled into a more or less thick paste. The paste is then scraped down towards one end of the filter and the cloth folded over. After allowing an hour or two for the liquid to drain still further, the pulpy mass, containing in this condition from 8 to 12 per cent. of indigotin, is ready for pressing.

Pressing and Cutting.—Each factory has a number of presses in operation. They stand upon heavy beams of timber or strong iron girders. The press consists of a strongly-made rectangular box, the framework having on all sides numerous perforations. The box is well-fitted with two thicknesses of strong, closely-woven cloth, and is arranged under a pair of powerful screws, which can be turned with long levers. The cloth is wetted and the paste from the table introduced into the box to a depth of 9 ins. to 13 ins., according to its consistency; the amount being regulated so as to obtain a pressed slab of 3 ins. to 3¼ ins. in thickness. The screws are turned very slowly at intervals extending over several hours. Unless great care is taken, the cloths burst and indigo is lost. When no more liquid is seen to be oozing from the block, the pressure is gently and evenly released. The slab, which now contains about 70 per cent. of water, is put on to a frame and cut by means of a brass wire into cubes of about 3 ins.

to 3¼ ins. in size. Each cube is stamped with the mark of the factory and the number of the day's boiling, and taken to the drying-house.

Drying.—The drying-house is a lofty, well-ventilated building, containing a number of shelves (about a foot apart) of light bamboo or wire netting. The cubes are placed on these shelves about half-an-inch apart, and left for a period of two or three months to dry. The drying takes place very slowly, as at this period of the year the humidity of the atmosphere is high. Strong currents of air are not permissible; or the cakes would crack and the value of the indigo in the Calcutta market be thereby much depreciated. There are usually a number of cakes broken, but the greatest care is taken to keep them whole. During the drying a considerable amount of ammonia is evolved, and the cakes become covered with a thick growth of fungus. It would appear from experiments which have been made that the ammonia and fungus are not produced at the expense of the colouring matter, but from the soluble extractive matter remaining in the cake after pressing. When dry, the cakes are brushed and packed into cases or chests, which are usually made of well-seasoned mango-wood.

Water used in Indigo Manufacture.—For the production of indigo an abundant supply of good water is indispensable; every pound requires from 300 to 500 gallons, and upon its quality largely depends the successful working of the operations. The chief sources of supply are river water, lake water, and rain water. The rivers of Behar generally flow from Nepal in the North, in a south-easterly direction, and empty themselves into the Ganges. The largest is the Gundak, on the West. Rain water is either collected in large tanks dug in the ground, or in natural depressions, forming "chowrs." Much of the soil in Behar is calcareous, and it frequently happens that the rain water in these tanks and chowrs contains as much mineral matter as the neighbouring river. Lake water varies greatly in composition, according to the rainfall. In times of drought, lake water often contains much organic matter in solution and suspension; such water is always considered to give bad results in indigo manufacture, both as regards produce and quality. Taking the average of about seventy samples, the water used for manufacturing indigo in Behar may be said to contain about 15 grains of solid matter per gallon, ranging from 4 to 28 grains. The hardness, which, almost without exception, is due to *carbonates* of lime and magnesia, averages 6°, with a maximum and minimum of 14° and 2° respectively. The majority of waters, however, only vary from 4° to 8° of hardness. Most of the waters, in addition to carbonates of lime and

magnesia, also contain small quantities of carbonate of soda. Sodium chloride is only present to the extent of about half a grain per gallon. With few exceptions, the waters are practically free from nitrates. On account of the heavy rains and the melting of snow in the Himalayas, the waters of Behar vary considerably in their composition from time to time. All planters agree that, other things being equal, fresh rain water is much the best for indigo manufacture, and that more or less stagnant water containing innumerable living organisms—vegetable and animal—is decidedly detrimental to the production of good indigo.

THE COLOUR-GIVING PRINCIPLE AND SOLUTION OBTAINED IN STEEPING.—Notwithstanding the great amount of time that has been devoted to the subject, it is not definitely known in what state of chemical combination the colour principle exists in the leaf of the plant nor the precise changes which take place during its conversion into indigo-blue. It was formerly considered that indigo-blue existed ready formed in the plant, and, at a later period, that it was present in the form of reduced indigo or indigo-white. Many years ago Dr. Schunck, in his classical researches on the "Formation of Indigo-Blue," proved both these views to be incorrect. He found the leaves of certain indigo-yielding plants—*Isatis tinctoria* and *Polygonum tinctorium*—to contain a peculiar compound which he named *Indican*. Dr. Schunck showed that when leaves of *Polygonum tinctorium* were placed in boiling alcohol, the principle was entirely removed and the leaf left of a yellowish-grey colour. When the vitality of the fresh leaf had been partially destroyed, by being punctured, or frozen, or treated with acid or cold spirits of wine and then immersed in boiling alcohol, those portions which had been affected became blue and the other portions were grey or colourless. Indican, which belongs to the class of bodies termed glucosides, is capable of being split up into indigo-blue and a kind of sugar. It has recently been shown that this change does not take place directly, and that indican itself does not contain the molecule of indigo-blue. It is highly probable that the colouring matter exists in the same form in the leaves of *Indigofera tinctoria* as in other indigo-yielding plants, but, as already stated, this has not been definitely proved. A theory of the steeping process which appears to obtain generally is that by fermentation the glucoside, indican, is decomposed into indigo-blue and a peculiar kind of sugar, and that the indigo-blue is then, by the action of further fermentation, reduced to indigo-white, which remains in solution until it is afterwards precipitated by oxidation in the beating vat. This simple view of the process, however, is not borne out by facts.

If the liquid running from the steeping vats contained indigo-white in solution it would be oxidised to indigo-blue in very much less time than is actually the case. Schunck and Römer * have shown that when indican is decomposed by hydrochloric acid in the absence of oxidising agents, a substance is produced which cannot be converted into indigotin; and further, that indigotin is formed from indican by the action of hydrochloric acid in the presence of an oxidising agent, and that these conditions — the presence of a hydrolysing agent and of an oxidising agent at the same time—are necessary for the production of indigotin. From the researches of these savants, Marchlewski and Radcliffe † have propounded the theory that indoxyl was the parent substance or origin of indigotin; and that the glucoside, indican, on hydrolysis yielded glucose and indoxyl. Dr. Ranking, in a paper read before the Asiatic Society of Bengal in 1896, also states that the liquid after steeping probably contains indoxyl, and not indigo-white, as had been formerly considered to be the case. Rawson's observations and experiments support this view. Indoxyl (C_8H_7NO) is a compound capable, like indigo-white, of being oxidised into indigo-blue, but for this change to take place it requires double the amount of oxygen needed for indigo-white.

Much difference of opinion prevails as to whether fermentation is necessary for the production of indigo-blue, or whether the fermentation is merely a result of the steeping process. It is possible to produce indigo-blue from the plant under such conditions that bacteria could not exist, and this would tend to show that fermentation was not a necessity. On the other hand, Alvarez professes to have discovered the micro-organism which produces the indigo fermentation. He cultivated the microbe (named *Bacillus indigogenus*) and found that it induced indigo fermentation in a sterilised extract of the leaves, which remained unaltered when freely exposed to the air without inoculation. Bréaudat ‡ attributes the formation of indigo to a "diastatic" fermentation, and not to the growth of a micro-organism. Van Lookeren Campagne § considers that the decomposition or transformation of indican takes place in the interior of the leaf by the action of bacteria; indigo-white diffusing into the liquid.

The liquid obtained on steeping the plant contains a number of substances—organic and inorganic—in solution, among which the most important, the indigo-forming principle, exists in very small proportion. An extract of indigo

* *Ber. d. deut. Chem. Ges.*, 1879, p. 2311.
† *Journ. Soc. Chem. Ind.*, May, 1898.
‡ *Comptes Rendus*, 1898, p. 769.
§ *Chem. Zeit.*, 1899, p. 16.

12

leaves has been variously stated to possess an acid, an alkaline, and a neutral reaction, but it has not been clearly stated what indicator was used for determining this condition. Many substances which exhibit an acid reaction to certain indicators are alkaline to others. This is the case with an extract of indigo leaves. Rawson found a fresh decoction of the plant to be neutral to both red and blue litmus paper. It was decidedly alkaline to methyl orange and acid to phenolphthalein. The liquid contains a large amount of lime, magnesia, and potash ; chiefly in combination with carbonic and organic acids. The solution obtained on steeping contains on an average about 0·55 per cent. of dry solid matter. This amount corresponds to 55 lbs. per 1000 gallons. Nearly one-half of the total solids consists of mineral matter ; bicarbonates of lime, magnesia, and potash predominating. The bulk of this matter, and practically the whole of the colouring matter, is derived from the leaves. Even the fine stems yield but traces of colour. The following table shows the relative amount of matter extracted from leaves and stems, when 100 grms. of each were separately steeped with ten times their weight of water in the usual manner. The plant contained 38 per cent. of leaf, and the results are also calculated for the whole plant.

E.—Matter extracted on Steeping Leaves and Stems separately.

	Leaves.		Stems.		Whole Plant.	
	In Liquid.	Calculated on Leaves.	In Liquid.	Calculated on Stems.	In Liquid.	Calculated on Whole Plant.
	p. ct.	p. ct.	p. ct.	p. ct.	p. ct.	p. ct.
Total solids, . . .	1·014	10·14	·185	1·85	·500	5·00
Mineral matter, . .	·263	2·63	·043	·43	·126	1·26
Alkalinity expressed as carbonate of lime, ...	·260	2·60	·080	·80	·148	1·48
Indigotin, ...	·052	·52	trs.	..	·020	·200
Indigotin expressed as a 60 per cent. indigo, ...	·086	·86	..	..	·033	·333

It will be observed that the indigotin only equals one twenty-fifth part of the total matter extracted from the plant. The amount corresponds to 5·33 ozs. of 60 per cent. indigo per 100 lbs. of plant. The average amount of indigo produced on a manufacturing scale per 100 lbs. of plant is about 4 ozs., but the figures vary greatly in different factories and also at different times in the same factory. In many cases the

variations are evidently due to the varying amount of leaf and stem constituting the plant, and it might naturally occur to one that it would be preferable to steep the leaves only. A process in which this idea was carried out was patented many years ago by Olpherts, but for some reason or other it has not been adopted.

If an alkali, such as lime, soda, or ammonia, be added to the liquid from the steeping vat, the carbonic acid, which is present in great quantities, is neutralised, and calcium and magnesium carbonates are precipitated. At the same time, the character of the indigo-yielding body appears to undergo a change, as it may now be readily oxidised to indigo blue ; in fact, the solution has all the appearances of a weak indigo-dyeing vat, containing indigo-white, or reduced indigo. The addition of alkalies has formed the subject of several patents. The want of success, however, has been due to the fact that the indigo thus obtained was necessarily contaminated with the precipitated lime and magnesium carbonates. In order to obviate this difficulty, B. Coventry introduced his system of using an intermediate vat, which retains the precipitated matter. If the liquid to be treated is perfectly clear, the precipitate obtained on the addition of an alkali consists almost entirely of mineral matter, but if it contains matter in suspension a considerable amount of organic matter is also removed. The indigo obtainable by Coventry's process is of very high quality, and it usually contains a very much greater proportion of indigo-red than indigo made in the ordinary way. The formation of indigo-red always occurs when an alkali is added in slight excess to the liquid from the steeping vat. This peculiar property was discovered by Schunck as long ago as 1855. The proportion of indigo-red formed appears to depend upon the amount of alkali added in excess, and the length of time occurring between this addition and beating. The production of indigo-red under these conditions is very strong evidence in support of the view that the liquid obtained on steeping indigo plant does not consist of a solution of indigo-white. Indigo-white is not changed into indirubin or indigo-red by the action of alkalies.

Various Methods Employed.—Innumerable patents have been taken out in India for improved methods of manufacture. In many cases extraordinarily good results are said to have been obtained, but, sooner or later, the "patent" method has been discarded, and the process of manufacture has fallen back into the ordinary routine, as already described. Improvement has been claimed at various times for the addition of hundreds of "chemicals," many of an oxidising character, some having reducing properties, some added with

a view of augmenting fermentation, and others for the purpose of arresting and preventing such action.

Of the great number of processes which have been patented, two or three only have been used on an extensive scale. Some fifteen years ago a method worked out by Michea, and which became known as the "*ammonia process*," gave every promise of becoming a success, but it has practically fallen into disuse. The indigo obtained was light and of a good colour. It usually contained a much higher proportion of indirubin than indigo made in the ordinary way,* but it also contained a large proportion of mineral matter. Indigo made by this process *appeared* to be of much finer quality than was found to be the case when submitted to analysis, or when actually used in dyeing. On this account, and also owing to its irregularity, it met with little favour among indigo buyers, and after a short run it became a drug in the market. In the specification, two methods of treatment are described, named respectively the "cold" and the "boiling" water processes. In the former treatment the plant is steeped in the ordinary way, and the solution obtained is at once heated to a temperature of 96° F. Ammonia (sp. gr. ·880) is added to the liquid, varying in amount according to the quality of the plant, in quantities up to 250 lbs. per 1000 cubic ft. of pressed plant. About 5 lbs. of nitrate of soda or of potash are also added, and the beating or oxidation proceeded with at once. Various methods of oxidation are described, among which is one of blowing in atmospheric air, or, preferably, ozonised air, by means of bellows, fans, or air pumps. It is further recommended that the temperature of the air blown in should be raised to that of the liquid.

In the *boiling* water process small shallow vats (2 ft. 6 ins. deep) are used. Water is run in and heated to the boiling point, and the indigo plant, in small loose bundles, introduced for a few minutes only. As soon as the scalding is complete, which is known by the liquid attaining a yellowish-green colour, the solution is rapidly drawn off into the beating vat. The requisite amount of ammonia is then added, and the liquor treated in the same manner as in the "cold water" process. Ammonia is said to unite with the indican, forming a body which is highly susceptible of oxidation, and which yields a far greater quantity of indigo than indican itself. In the ordinary steeping vat ammonia is produced by the fermentation of the nitrogenous substances present in the indigo plant, but not in sufficient quantity to combine with and convert the whole of the indican into the more readily oxidisable body, which afterwards yields indigo-blue. In the ordinary

* Rawson, *Journ. Soc. Dyers and Col.*, 1886, p. 141.

process of manufacture, therefore, there is always a loss from a portion of the indican escaping conversion into indigo-blue. The ammonia added, as previously described, effects the complete oxidation and decomposition of the indican, thus utilising the whole of the indigo-producing bodies present in the plant.

It has already been pointed out that when an alkali is added to the liquid obtained on steeping indigo plant in water a precipitate, consisting principally of carbonates of lime and magnesia, is produced. Much of the increase in weight obtained by following the ammonia process was no doubt due to this cause, though an actual increase of colouring matter was also obtained. In Coventry's process an alkaline body—preferably lime, on account of its cheapness—is also used, but in this case the precipitated carbonates are removed by subsidence, in a vat placed between the steeping and beating vats. Each steeping vat has a corresponding precipitating vat. The requisite amount of lime (200 to 250 lbs. per 1000 cubic ft. of pressed plant) is placed in a small tank or box fixed just above the outlet of the steeping vat. It is mixed with water, and the milk of lime thus formed is allowed to run into the precipitating vat simultaneously with the liquor run out of the steeper. If mixed afterwards, oxidation takes place and indigo is lost. The precipitate produced and the impurities in the lime soon settle, and after half an hour or so the supernatant liquid is run off into the beating vat and treated in the usual way. Oxidation takes place rapidly, and usually in the course of about half an hour the beating operation is complete. Although the great bulk of the lime is left in the "precipitator," in some cases the indigo produced by this process contains a large amount of mineral matter, chiefly lime. For the successful working of the operation it is, therefore, necessary to use an acid. Coventry adds the acid to the "mal" in the boiler, after running off as much of the clear waste water as possible. He recommends from 25 to 30 lbs. of hydrochloric (or a corresponding amount of sulphuric) acid per 100 lbs. of indigo treated. The exact amount of acid necessary may be determined by means of blue litmus paper. As already stated, the indigo obtained by this process is of very high quality, and it usually contains a high percentage of indirubin or indigo-red. According to Coventry, this excess of indirubin is produced in place of the brown matters formed in larger or smaller quantities in the ordinary course of manufacture. A drawback to the process is that the amount of indirubin formed is not a constant quantity, but no doubt this difficulty may be overcome by further experience. A process recently patented by

Dr. Ranking consists in adding sodium peroxide to the liquid before beating, in the proportion of about 6 lbs. per 1000 cubic ft. of pressed plant. Oxidation naturally takes place much more quickly, and it is claimed that an increase of colouring matter to the extent of 10 to as much as 80 per cent. is obtained.

Dry Leaf Process.—In some parts of Madras indigo is made from the dried leaves instead of from fresh plant. The ripe plant is cut in dry weather an hour or two before sunset, and then dried in the sun on two consecutive days between 9 a.m. and 4 p.m. When dry the plants are submitted to a process of threshing, so as to separate the leaves from the stems. The leaves in the course of a few weeks undergo a change in colour; their beautiful green tint turning to pale bluish-grey. The leaves are now ready for extraction. They are put into a steeping vat with six times their bulk of water and macerated for two hours, with continual stirring till all the floating leaves sink. The fine green liquor is then drawn off into the beating vats without delay, and treated in the ordinary way.

Instead of steeping in the usual manner for eight to twelve hours, a short maceration in hot water has frequently been tried, but although in some cases good results have been obtained the process has not been adopted in India. It is said that new and improved methods of manufacture have recently been introduced into Java, and that the colouring principle has been extracted from the plant by means of hot water. It would also appear that some alkali was used in the operation, since Java indigo now frequently contains much indirubin, whereas formerly it contained very little. Many samples of Java indigo have recently been found to contain a yellow colouring matter. Further reference to this peculiarity will be found on page 195, under *Analysis of Indigo.*

At the present time various new methods of manufacture are being tried in Bengal, but the details cannot be discussed until the experiments are complete.

CONSTITUENTS OF INDIGO.

Indigotin is by far the most important constituent of natural indigo. Its proportion varies greatly—from 5 to 80 per cent. Good Bengal indigo may be said to contain on an average from 60 to 66 per cent. Madras indigo, on the whole, is of inferior quality. It contains on an average about 30 per cent., but the variations are much greater than in the case of Bengal indigo. Some qualities contain upwards of 50 per cent. Broadly speaking, the indigo made in the North-West Provinces (Oude, &c.) is of a quality intermediate between that of Bengal and Madras.

Java indigo contains, as a rule, the highest percentages of indigotin, but the general opinion of woollen dyers in England is that it does not give such good results as a high-class Bengal product of a corresponding quality. Indigo also contains another colouring matter of considerable tinctorial value—viz., indirubin or indigo-red. Until comparatively recently, this constituent was rarely present beyond 2 per cent., but at the present time commercial indigo frequently contains as much as 10 per cent. and upwards.

In addition to indigotin and indirubin, natural indigo contains a variety of other substances which are usually regarded as impurities, though in some cases the organic matters undoubtedly have an appreciable effect in dyeing. They comprise indigo gluten and various brown substances, and amount in all to about 20 to 30 per cent. Natural indigo always contains more or less mineral matter. This is partly derived from the leaves of the plant, and partly from suspended matter (clay and sand) present in the water used for steeping. The amount of mineral matter found in natural indigo varies greatly from 2 or 3 per cent. to 60 per cent., and even more. Good Bengal indigo usually contains from 3 to 6 per cent.

INDIGOTIN, $C_{16}H_{10}N_2O_2$, may be prepared in a pure state in a variety of ways. A simple method consists of gently heating a little powdered commercial indigo in a platinum dish or tray covered with another dish of the same size. The indigotin sublimes or condenses on the surface of the upper dish in beautiful needles of a purple colour. It may also be obtained by boiling finely-powdered indigo with aniline, filtering whilst still hot, and allowing the liquid to cool, when indigotin crystallises out. After washing with alcohol the product is pure indigotin.

Another method which gives very good results is known as Fritzsche's process, and may be carried out in the following manner:— 5 grammes of very finely-powdered indigo, 10 grammes of pure grape sugar, 50 c.c. of a 40 per cent. solution of caustic soda, 150 c.c. of water, and 300 c.c. of 90 per cent. alcohol, are put into a flask fitted with a cork and syphon tube. The mixture is heated on a water-bath for half an hour, and the insoluble matters are allowed to subside. The clear liquid is syphoned off, and a current of carbon dioxide passed through it, and then a current of air. Indigotin is thereby precipitated; it is collected on a filter, washed (1) with dilute hydrochloric acid, (2) with water, and then dried.

Pure indigotin crystallises in beautiful dark-blue or purple needles, which exhibit a coppery reflex. The powder, which is of a deep blue colour, assumes a bright red bronzy appearance when burnished. Indigo begins

to sublime, according to Schunck, at 170° C.; but other authorities give a much higher subliming point. The vapour possesses a beautiful red-violet colour, resembling that of iodine. In the open air, although the greater portion of the indigotin sublimes, it is partially decomposed, leaving a mass of porous carbon. In an inert gas it may be volatilised without decomposition. When submitted to dry distillation—that is, heated in a closed vessel, either alone or with an alkali—indigotin is decomposed, the chief product being aniline.

Indigotin is a neutral body, and is insoluble in water, ether, dilute acids, and alkalies. It is slightly soluble in boiling alcohol with a blue colour, but is again deposited on cooling. Amylic alcohol, carbolic acid, chloroform, and carbon bisulphide also dissolve small quantities when hot, but the best solvents for indigotin are glacial acetic acid, nitrobenzene and aniline. Boiling paraffin dissolves indigotin with a magenta colour. Concentrated sulphuric acid completely dissolves indigotin, but since its composition is changed, under these conditions sulphuric acid cannot be considered a solvent for indigotin as such. Glacial acetic acid containing a few drops of sulphuric acid dissolves indigotin with a deep blue colour, and on dilution with water it is reprecipitated unaltered.

By the action of oxidising agents, such as dilute nitric acid, chromic acid, &c., indigotin is converted into *isatin* or indigotic acid. If nitric acid is used hot, it forms *nitro-salicylic acid* or *picric acid*, according to the strength of the acid. At the same time other products, such as carbonic acid and oxalic acid, are formed.

By the action of certain bodies, termed "reducing agents" (compounds capable of giving up nascent hydrogen or assimilating oxygen), indigotin is converted into a colourless compound known as *indigo-white* or *reduced indigo*. This body is soluble in alkaline liquids, such as lime, potash, or soda. It is in this form that indigo is used for vat dyeing. The material to be dyed is immersed in a vat containing reduced indigo; this, on exposure to the air, is oxidised to indigotin, which is thus fixed in the insoluble form on the fibre.

There are numerous substances which have the power in alkaline solution of reducing indigo-blue to indigo-white — *e.g.*, sodium amalgam, zinc, tin, aluminium, magnesium, &c.; sulphide of arsenic, ferrous hydrate, hyposulphurous and hypophosphorous acids; glucose, gallic acid, &c., and certain organic ferments. Reduced indigo is a greyish-white amorphous powder, insoluble in water and dilute acids, but soluble in alcohol and ether, and in alkaline solutions; the powder, on exposure to air, oxidises to blue indigotin;

the change takes place rapidly in the presence of water. An alkaline solution of reduced indigo has a brownish-yellow colour; an excess of the reducing agent gives a clear, bright yellow solution. On exposure to the air, this becomes at first green, then blue, and is covered with a bronzy scum which consists of minute crystals of indigotin. If an oxidising agent, such as potassium bichromate, be added to the solution, the blue colour of indigotin is at once developed. An alkaline solution of reduced indigo gives bulky white precipitates with salts of alumina, zinc, magnesia, and the proto-salts of iron, lead, and tin. The tin compound was formerly used in calico printing. Reduced indigo forms two compounds with lime, one of which is soluble and the other insoluble.

INDIGOTIN SULPHONIC ACIDS. — It has already been stated that indigotin dissolves in concentrated sulphuric acid, thereby undergoing a change in its composition. According to the condition, either mono- or disulphonic acid is formed.

Indigotin monosulphonic acid, also known as sulphopurpuric acid and indigo-purpuric acid, is obtained by mixing 1 part of indigotin with 4 parts of concentrated sulphuric acid, and allowing the mixture to stand not more than half an hour, when it is diluted with water. A beautiful purple precipitate is formed which is only sparingly soluble in water. The sodium salt is used in dyeing, under the names of indigo-purple, red extract of indigo, and red indigo-carmine.

Indigotin disulphonic acid, also known as sulphindigotic acid, is obtained by treating indigotin with a larger proportion of sulphuric acid, and allowing it to act for a longer time, or by heating the mixture, or by both combined. One part of indigotin treated with 10 or 12 parts of concentrated sulphuric acid at a temperature of 90° C. is converted into sulphindigotic acid in about half an hour. At the ordinary temperature it is necessary to allow the mixture to stand for ten or twelve hours. On diluting with water, the sulphonic acid remains in solution, being soluble in about 60 parts of water. If any sulphopurpuric acid is present, it is precipitated in the form of a purple powder. The pure sulphonic acid may be obtained by adding a saturated solution of common salt, which produces a precipitate of sodium sulphindigotate. The precipitate is collected on a filter and washed with a saturated solution of salt, in order to remove free acid. The paste is then dissolved in water and the solution precipitated by lead acetate. The insoluble lead salt is washed and decomposed by sulphuretted hydrogen. The solution freed from lead sulphide yields on evaporation, pure sulphindigotic acid. It is insoluble in alcohol.

Sulphindigotic acid, or indigo sulphate, as it is often termed, is decolourised by reducing agents in a similar manner to indigotin itself. The colourless solution becomes blue again on exposure to air. By the action of oxidising agents, such as potassium bichromate and potassium permanganate, it is converted into sulphisatic acid. Both these series of reactions are utilised for the estimation of indigotin in commercial indigo.

Sulphindigotic acid is decomposed by strong solutions of caustic alkalies, forming at first a green and ultimately an orange-coloured solution. Weak solutions and alkaline carbonates form sulphindigotates, which are soluble in water, but very sparingly soluble in strong saline solutions.

The potassium salt dissolves in about 150 parts of water, and the sodium salt is somewhat more soluble. The lead salt is insoluble, and the barium salt is only very sparingly soluble.

Strong ammonia, added to a solution of sodium sulphindigotate, produces a green colour, which is named by V. H. Soxhlet* indigo - green. The product has not been thoroughly investigated. It may be simply a mixture of a sulphindigotate and some yellow decomposition product.

Indigodisulphonic acid may be prepared synthetically by the action of fuming sulphuric acid on phenylglycocol and in other ways.†

Indigotin Sub-sulphonic Acid. — Gerland‡ describes the formation and properties of *indigotin sub-sulphonic acid,* which he obtained by treating indigo with sulphuric acid of a specific gravity of 1·6 to 1·7. In the cold, the action proceeds very slowly, but, immersed in boiling water, solution is effected in from one to three hours. On addition of water to this liquid the sulphonic acid compound is completely precipitated and may be collected on a filter, washed with weak hydrochloric acid, pressed and dried. This new body is of a dark violet-blue colour. It falls to powder by gentle pressure, and when rubbed does not take a metallic lustre like indigo. It is not changed by heating to 120° C.; at higher temperatures violet vapours are evolved. The substance dissolves slowly and only partially in water, with a blue colour. It is not a definite chemical compound but evidently a mixture of several subsulphonic acids, since the percentage of sulphur present varies according to the mode of formation. It is always less than that contained in indigomonosulphonic acid. The more sulphur there is present the more soluble is the body in water. Boiling nitrobenzene dissolves a portion of the body, and, on cooling,

crystals are obtained which are indistinguishable from indigotin, except that they contain sulphur and are slightly soluble in benzene with a blue colour. Caustic alkalies and hydroxides of the alkaline earths destroy the compound even in weak solution, with change of colour from blue to yellow. Strong nitric acid acts violently, yielding a red solution. Hydrogen peroxide or ammonium persulphate acts in presence of alkali, but in acid solution a reaction only becomes perceptible after long contact.

Marchlewski and Radcliffe, in the *Journal of the Society of Chemical Industry* (1898, p. 432), describe the formation and preparation of di-isatic acid (or O'Neill's acid) * prepared from indigo by oxidation with permanganate in the presence of glacial acetic acid and subsequent hydrolysis with caustic soda.

ARTIFICIAL INDIGOTIN.—After many years of labour, artificial indigo was introduced into the market under the name of "indigo pure" in July, 1897, by the Badische Anilin and Soda Fabrik. Indigotin had previously been produced synthetically in a variety of ways, but the cost of production was far above that of the natural product. Baeyer's name will always remain inseparably connected with the synthesis of indigo. In 1870, Baeyer and Emmerling succeeded in producing indigotin from isatin, but the synthesis was not complete until 1878 when the former chemist obtained isatin from indoxyl, and in conjunction with Suida prepared, in its turn, indoxyl from orthoamidophenylacetic acid. In 1880, Baeyer obtained indigotin in various ways from cinnamic acid.

One method may be briefly summarised as follows : —

(*a*) Formation of orthonitrocinnamic acid.

(*b*) Treatment with bromine whereby orthonitrodibromhydrocinnamic acid is produced.

(*c*) By action of caustic alkali orthonitrophenylpropiolic acid is obtained.

(*d*) Reduction with glucose or xanthates when indigotin is formed.

In 1882, Baeyer and Drewsen obtained indigotin from orthonitrobenzaldehyde by treating this compound with acetone or acetic aldehyde in the presence of caustic alkali. In this reaction orthonitrophenyl lactone is formed as an intermediate product. In 1893, Kalle & Co. introduced their "indigo salt," which consists of the above-named body in combination with sodium bisulphite. It is readily soluble in water, and yields indigotin at once on the addition of caustic soda.

In 1890, details of Heumann's synthesis of indigo from phenyl glycocol were published. When heated with caustic alkalies to a temperature of 250° C. phenylglycocol is

---

* *Chem. News,* vol. lxiv., p. 85.
† Heymann, *Journ. Soc. Chem. Industry,* 1891, p. 827.
‡ *Journ. Soc. Chem. Industry,* 1899, p. 225.

* *Manchester Literary and Philosophical Society's Proceedings,* 1892.

converted into pseudoindoxyl, which, on oxidation, yields indigotin. This process, together with several others for the production of indigotin and intermediate compounds, is in the hands of the Badische Anilin and Soda Fabrik. The exact method employed by this firm for the manufacture of indigotin, or "indigo pure," is not known, but it is said to be obtained from naphthalene and carried out in the following stages :—

1. $C_{10}H_8$ Naphthalene   → to $C_6H_4 \begin{cases} COOH \\ COOH \end{cases}$ Phthalic acid.

2. $C_6H_4 \begin{cases} COOH \\ COOH \end{cases}$ Phthalic acid   → to $C_6H_4 \begin{cases} CO \\ CO \end{cases} NH$ Phthalimide.

3. $C_6H_4 \begin{cases} CO \\ CO \end{cases} NH$ Phthalimide   → to $C_6H_4 \begin{cases} COOH \\ NH_2 \end{cases}$ Anthranilic acid.

4. $C_6H_4 \begin{cases} COOH \\ NH_2 \end{cases}$ Anthranilic acid   → to $C_6H_4 \begin{cases} COOH \\ NHCH_2COOH \end{cases}$ Phenyl-glycin orthocarboxylic acid.

5. $C_6H_4 \begin{cases} COOH \\ NHCH_2COOH \end{cases}$ Phenyl-glycin orthocarboxylic acid   → to $C_6H_4 \begin{cases} CO \\ NH \end{cases} CHCOOH$ Indoxyl carboxylic acid.

6. $C_6H_4 \begin{cases} CO \\ NH \end{cases} CHCOOH$ Indoxyl carboxylic acid   → to $C_6H_4 \begin{cases} CO \\ NH \end{cases} C = C \begin{cases} CO \\ NH \end{cases} C_6H_4$ Indigotin.
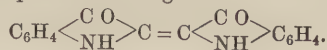
Synthetic or artificial indigotin possesses the same chemical and dyeing properties as indigotin prepared from natural indigo. The two indigotins may be considered to be identical. Marchlewski and Radcliffe [*] have studied the acetyl oxidation products obtained from indigotin, from Kalle's salt, indigo pure of the Badische Anilin and Soda Fabrik, and indigotin from natural indigo. In all cases identically the same results were obtained.

INDIRUBIN, or indigo - red, possesses the same empirical formula as indigotin—viz., $C_{16}H_{10}N_2O_2$.

Schunck and Marchlewski [†] have shown that it is the indogenide of isatin and has the constitution—

$$C_6H_4 \begin{cases} CO \\ NH \end{cases} C = C \begin{cases} C_6H_4 \\ CO \end{cases} NH$$
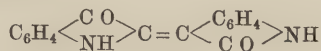
as compared with indigotin—

$$C_6H_4 \begin{cases} CO \\ NH \end{cases} C = C \begin{cases} CO \\ NH \end{cases} C_6H_4.$$

It has been previously stated that when indican is submitted to fermentation, or treated with dilute acids, it splits up into indigotin and sugar. This indican is very susceptible of alteration, and its modifications yield, according to existing conditions, either indirubin or indiretin and indihumin, the latter two bodies forming indigo - brown. Schunck found that when indican was mixed with caustic soda and allowed to stand for some days the solution yielded indirubin but no indigotin. Indican thus modified by the

* Journ. Soc. Chem. Industry, 1898, p. 433.
† Ber. d. deutschen Chem. Ges.. 1895, p. 539.

action of caustic soda was named by Schunck indicanin.

Indirubin is said to be formed in larger quantities than usual when indican is decomposed by oxalic or tartaric acid. It may be obtained from commercial indigo by extraction with alcohol, ether, or glacial acetic acid, indigotin being insoluble in the cold. The indigo should, in the first case, be boiled with dilute hydrochloric acid, and washed with water. A hot concentrated solution of indirubin in alcohol deposits the indirubin on cooling in the form of microscopic bundles of dark purple - coloured needles. Indirubin sublimes at a lower temperature than indigotin, and condenses again in the form of beautiful crimson needles. It is unaffected by weak acids and alkalies, but, like indigotin, is reduced to a colourless compound soluble in alkalies by the action of substances yielding nascent hydrogen. Wool or cotton immersed in such a solution and then exposed to the air becomes dyed a fast purple colour. Indirubin is soluble in alcohol, ether, acetone, and glacial acetic acid. It dissolves in concentrated sulphuric acid, forming a deep crimson solution, which produces no precipitate on dilution with water. This solution is oxidised but slowly by potassium permanganate or bichromate. If solutions of indigotin and indirubin sulphonic acids be mixed together and titrated in the cold with potassium permanganate the whole of the blue compound is decomposed (decolourised) before the red is affected. On slowly continuing the addition of potassium permanganate, the colour of the solution passes from a crimson

to a bright scarlet, and then through various shades of orange to a bright yellow.

Indirubin dyes wool and cotton crimson shades which are exceedingly fast to light. The sulphonic acid of indirubin is much faster than the corresponding indigotin compound. When dyed on wool indirubin gives the following reactions :—

Reagent.	Indirubin-Sulphonic Acid.	Indirubin, dyed in the " Vat."
Hydrochloric acid — conc. (cold).	No action.	No action.
Sulphuric acid— conc (cold).	Fibre redder.	Solution crimson.
Nitric acid— conc. (cold).	Fibre yellow.	Liquid and fibre at first crimson, slowly turning yellow.
Sodium hydrate —10% (cold).	Decolourised.	No action.
Ammonium hydrate—sp. gr. ·880 (cold).	Little action.	No action.
Sodium carbonate—1% (boiling).	Colour extracted.	No action.
Soap solution— 1% (boiling).	Little action.	Little action.
Alcohol (boiling).	No action.	Colour extracted ; solution deposits microscopic needles.

ARTIFICIAL INDIRUBIN. — Like indigotin, indirubin can also be made synthetically, and has been put on the market to a limited extent by the Badische Anilin and Soda Fabrik. Baeyer obtained it by the action of indoxyl on isatin, and it is also produced along with indigotin by the reduction of isatin chloride. Much difference of opinion exists regarding the identity of natural and artificial indirubin. Koppeschaar [*] states that the carmine of synthetic indirubin is readily soluble in strong salt solution ; that of natural indirubin being nearly insoluble. Rawson, however, has found that both carmines are alike nearly insoluble in salt solution, a fact which had also been observed by Marchlewski.

The constitution of synthetic indirubin was first established by Baeyer, but the formula he proposed has since been slightly altered by Schunck and Marchlewski,[†] who have shown natural and artificial indirubin to be identical. Later, Marchlewski and Radcliffe [‡]

* Zeit. für Anal. Chem., 1899, p. 1
† Berl. Ber., 1895, p. 539.
‡ Journ. Soc. Chem. Industry, 1898, p. 434.

have found synthetic and natural indirubin to behave in exactly the same manner under similar conditions. They found that indirubin was only partially converted into indigotin in the presence of *alkaline* reducing agents, whereas complete conversion took place when it was treated with *acid* reducing agents. In face of the convertability of indirubin into its blue isomer, and on account of the small quantity of indirubin present in natural indigo, they consider the importance frequently ascribed to indirubin in dyeing to be over-estimated. On the other hand, however, indirubin, when present to an appreciable quantity in indigo, has been found by actual practice to be of much value—particularly in wool-dyeing,

Principally for the sake of economy, but also for other reasons, a red colouring matter, such as cudbear, camwood, &c., is frequently used in indigo dyeing, and indirubin is eminently suited for this purpose. It is true that until comparatively recently natural indigo rarely contained more than 1 or 2 per cent. of indirubin, but, as previously stated, much indigo now contains as much as 10 per cent. and upwards.

INDIGO GLUTEN may be removed from natural indigo along with some of the mineral matter by treatment with dilute acid. It is a yellowish-brown amorphous glue - like substance possessing properties similar to ordinary vegetable gluten. In cotton-dyeing it acts advantageously in making the colour faster to washing.

INDIGO - BROWN. — The brown substances present in indigo are named by Schunck *indiretin* and *indihumin*. When a solution of indican is heated for some time and then treated with an acid, it yields neither indigotin nor indirubin, but a dark brown precipitate consisting of the above two bodies, which are invariably present to a greater or less extent in commercial indigo.

The brown matter dissolves in caustic soda, and a portion of it is precipitated on neutralising the liquid with an acid. It dissolves in concentrated sulphuric acid with a deep dark brown colour, but is entirely precipitated on dilution with water. Schunck [*] describes the formation of five brown compounds derived from indigo-blue. Under certain conditions one or more of these compounds may be formed during the process of manufacturing indigo.

Applications of Indigo.

Indigo is a substantive dye, and consequently requires no mordant. It is used very largely both in wool and cotton dyeing. In addition to the dyeing and printing of blue, indigo is used to a very great extent as a bottom for compound shades. Such shades

* Memoirs of the Lit. and Phil. Soc. of Manchester, 1864-5.

(browns, olives, blacks, &c.), which contain indigo, are said to be *woaded*. In most cases the cloth or other material is dyed with indigo first, and then filled up (mordanted if necessary) with the other colouring matters. In any case the indigo requires a special vat. As previously stated, indigo is applied to the textile fibres in the form of indigo-white or "reduced indigo," soluble in alkalies. Many of the substances already mentioned as being capable of transforming indigo-blue into indigo-white are utilised on the large scale for the dyeing of indigo. For the dyeing of wool the vats are usually heated to a temperature of about 50° C. Cotton and other vegetable fibres are generally dyed cold.

The following are the most important indigo vats:—

Woad vat, ...
Soda or German vat, . . . } Used in
Potash vat, ... } wool dyeing.
Hyposulphite or "hydrosulphite"
vat, ... } Used in
Copperas vat, ... } cotton
Zinc vat, ... } dyeing.

The Indigo Trade.

The indigo crop is greatly dependent upon the weather; hence we find great variations in the exports from year to year. Notwithstanding the severe competition of coal-tar colours during the past ten or twenty years,

the exports of indigo from India have not materially changed. It is true that for many styles of dyeing, coal-tar colours have largely replaced indigo, but the amount thus replaced appears to have been compensated by the opening up of new channels or by the general increase in the trade of the textile industries throughout the world. Probably the consumption of indigo has been most affected by the introduction of acid colours, which have to such a great extent superseded extract of indigo. Indigo extract differs essentially from indigo itself. It is the sulphonic acid compound of indigo, and unlike the original colouring matter, is neither fast to light nor milling.

Although indigo has been cultivated in India for many centuries, the amount imported from the whole of Asia into Great Britain in 1782 was only 25,500 lbs. In the same year the States of America and the West Indies furnished 225,500 lbs. The total imports amounted to 495,000 lbs. From that year the imports steadily increased; in 1795 they amounted to 4,368,000 lbs., of which Bengal alone furnished 2,955,000 lbs. In 1815 the indigo exported from Bengal amounted to 7,650,000 lbs., or rather more than 3500 tons.

The following table shows the amount of indigo exported from India from 1877 to 1897 and the distribution of the crop:—

F.—Showing Amount of Indigo (in cwts.) Exported from India from 1877 to 1897, and its Distribution.

Years ending 31st March.	Exported from Bengal.	Exported from Madras, Bombay, and Sindh.	Total.	Distribution.						
				United Kingdom.	United States.	Germany.	Austria, France, and Italy.	Egypt and Turkey.	Persia.	Other Countries.
1877,	69,379	30,987	100,366	61,141	6,157	..	19,292	..	2,961	18,833
1878,	99,402	21,203	120,605	51,641	9,832	..	38.009	12,417	4,152	4,554
1879,	74,747	30,304	105,051	52,552	10,773	..	22,966	8,637	4,354	5,769
1880,	47,928	52,995	100,923	56,783	13,408	..	15,622	9,248	4,116	1,746
1881,	88,111	28,759	116,870	60,092	10,074	..	24,937	18,037	3,024	706
1882,	91,898	58,465	150,363	81,504	19,935	..	27,830	14,792	5,510	702
1883,	99,715	41,326	141,041	60,645	27,285	..	25,514	20,109	6,077	1,411
1884,	110,015	58,575	168,590	93,386	21,194	677	29,799	16,346	4,593	2,595
1885,	106,069	48,560	154,629	71,870	25,082	4,026	26,621	18,064	5,824	3,052
1886,	76,109	56,386	132,495	64,204	20,737	3,196	24,051	14,194	3,909	2,204
1887,	87,941	50,455	138,396	53,152	28,133	4,596	23,538	18,398	7,445	3,144
1888,	87,335	52,309	139,644	56,986	21,350	6,392	28,186	15,996	5,229	4,505
1889,	86,701	55,746	142,447	59,762	25,123	8,088	22,486	16,628	5,022	5,338
1890,	91,835	65,281	157,116	68,205	22,478	9,805	24,371	15,815	10,423	6,019
1891,	69,819	48,606	118,425	53,373	13,085	7,029	18,262	17,182	6,139	4,355
1892,	98,075	27,252	125,327	38,277	20,278	11,755	24,992	18,685	5,333	5,987
1893,	61,637	65,066	126,703	58,086	18,917	4,381	20,401	14,899	4,212	5,807
1894,	76,398	55,001	131,399	52,578	12,131	12,572	24,630	16,662	6,622	6,204
1895,	106,830	59,478	166,308	50,996	26,044	14,414	30,132	21,966	10,599	12,157
1896,	111,714	75,623	187,337	66,215	21,094	16,929	38,658	16,664	5,014	22,763
1897,	109,001	60,543	169,543	62,669	22,492	11,816	26,772	15,467	3,663	26,644

According to the Board of Trade Returns, the value of the indigo imported into Great Britain far exceeds that of all the aniline and alizarin colours of every description.

Northern Behar, which comprises the district of Tirhoot, Chumparan, and Chuprah, furnishes about two-fifths of the total amount of indigo produced in India. From 250,000 to

300,000 acres of land are devoted to the culti-
vation of the plant, and some million and a
half of people are employed in the industry.
The capital there invested is about £5,000,000
sterling.

Analysis of Indigo.

The technical journals devoted to dyeing
and to the chemistry of dyes, &c., have of
late years contained numerous articles on the
analysis and testing of indigo.   Formerly
indigo was generally bought and sold without
any pretence at analysis, but during the past
few years a change in this respect has been
taking place.   No doubt, in course of time
the price of different qualities of indigo will
be governed entirely by the percentage of
colouring matter contained therein.

The value of dyes as a class is ascertained
by making comparative dye-trials.   It is only
in a few cases that methods of chemical anal-
ysis are used.   Indigo stands out prominently
as one of these exceptions.   Unless the colour-
ing matter in a dyestuff can be readily deter-
mined with a fair degree of accuracy, the
method of valuing by comparative dye-trials
is much to be preferred.   It should be borne
in mind, however, that the experimental error
involved in making dye-tests is great in com-
parison with that of an ordinary chemical
analysis.   Even under the most favourable
conditions, the eye is incapable of discrimi-
nating between two shades of the same colour
if the difference is less than a certain small
amount, which in a chemical analysis would
be considered great.

It has often been recommended to test
samples of indigo by means of dye-trials in
small vats in a similar manner to the dyeing
of indigo on a large scale ; the zinc or hypo-
sulphite vat being the one usually recom-
mended.   The results, however, are untrust-
worthy.   It is almost impossible to secure
identical conditions in the several small vats
employed, and the slightest variation is suffi-
cient to cause a great difference in the depth
of shade obtained.   Two tests made with the
same quantity of the same sample rarely come
out the same ; very often the difference is great.
A much better method of making dye-trials
with indigo, and one which gives fairly good
results, is to dye swatches of woollen cloth or
yarn with the indigo disulphonic acid.   For
this purpose 0·5 grm. of the sample is dissolved
in 20 c.c. of concentrated sulphuric acid and
diluted with water to 500 c.c.   10 grms. of wool
are then dyed with 50 c.c. of this solution and
compared at the same time with a standard
sample.   Fairly good results may be obtained
by making colorimetric tests with these solu-
tions, which, however, must be filtered from
the dark green insoluble matter usually pre-
sent.   But even after filtering, solutions ob-
tained from various indigoes often possess

very different shades, on account of varying
quantities of impurities present ; and, when
this is the case, it is very difficult to arrive at
satisfactory results.   This difficulty, however,
may be removed by precipitating the colour-
ing matter with salt and redissolving it in dis-
tilled water.

The methods employed for testing indigo
may be broadly classified into four groups—
   1. Conversion into indigo sulphonic acid.
      (a) Indigotin estimated by oxidation.
      (b)   ,,   ,,   ,, reduction.
   2. Indigotin reduced in an alkaline solu-
tion ; the indigotin re-oxidised, separated,
purified, and weighed.
   3. Sublimation.
   4. Extraction by volatile solvents.
   PREPARATION OF THE SAMPLE.—In the first
place it is, of course, important that the
composition of the sample taken for analysis
should represent as nearly as possible that of
the bulk from which it has been obtained.
Until dealers and consumers fully appreciate
the great importance of accurately sampling
chests of indigo they will always be inclined
to look upon chemical analysis with a certain
amount of distrust.   Very often a single
piece of indigo is sent for analysis.   Some-
times three, four, or five lumps, representing
fifteen or twenty chests, are sent.   Perhaps
after some time another sample from the
same bulk is submitted, and the senders ex-
press surprise if it does not come out exactly
the same as the first one.   It is true that in
the finer qualities of indigo there is little
variation in the cakes or lumps forming a
chest, or, indeed, in a string of chests, but in
low and medium Kurpahs the variation is
often very great.   It is frequently possible to
pick out from a chest of indigo pieces varying
in colouring matter to the extent of 10 per
cent.   In order to arrive at an approximate
valuation of such chests it is evident that the
testing of one or two pieces only is of little or
no use.   The testing sample is prepared by
taking small pieces from each of the lumps in
the sample and pounding them together in a
mortar.   After grinding a portion to a pow-
der, it is passed through a fine sieve, and
any particles remaining are returned to the
mortar until the whole of the sample will
pass through the sieve.   It is particularly
important that the indigo should be extremely
fine when processes in group 2 are employed.

In the *Journal of the Society of Dyers and
Colourists*, 1885, pp. 74 and 201, Rawson
gives a description of various methods of
indigo testing.[*]   From these papers, and

---

[*] See also Helen Cooley, *Journ. Anal. Chemistry*,
vol. ii., p. 129 ; E. v. Cochenhausen, *Leipziger Monat.
für Textil-Industrie*, vol. iii., p. 406 ; F. Ulzer, *Mitth.
des k. k. Technol. Gewerbe - Museums* — abstract in
Journ. of Soc. Dyers and Col., 1891, p. 183 ; *Allen's
Commercial Organic Analysis*, as well as the various
references mentioned in the text.

others since published by him, the following processes are, unless otherwise stated, chiefly taken.

Dissolving the Indigo in Sulphuric Acid.— Various methods have been recommended for dissolving the sample in acid, but the following has been found to give the most satisfactory results.

Half a gramme of finely-powdered indigo is intimately mixed in a small mortar with its own weight of ground glass. The mixture is gradually and carefully added, during constant stirring with a glass rod, to 20 c.c. of concentrated sulphuric acid contained in a cylindrical porcelain crucible (cap. 30 c.c.); the mortar is rinsed out with a little powdered glass, which is added to the contents of the crucible, and the whole is exposed in a water-oven for a period of three-quarters to one hour to a temperature of about 70° C. The sulphindigotic acid thus formed is diluted with water, made up to 500 c.c., and the liquid filtered in order to separate certain insoluble impurities, which would otherwise interfere with subsequent operations.

Pure indigo-blue, dissolved in sulphuric acid, is, by the action of various oxidising agents, more or less readily converted into a pale yellow body named sulphisatic acid. The substances which have been most generally used for the purpose of analysis are chlorine, bichromate of potash, and permanganate of potash.

(a) *Potassium Permanganate Method.*—Of all the processes depending on the oxidation of indigo this is by far the best. It is important (as it is in all other cases) to operate upon very *dilute* solutions, otherwise the end of the reaction is obscured by the dark colour of the liquid. This fact has been overlooked by many writers, and has been the cause of bringing the permanganate method into disrepute.

The following mode of procedure is recommended:—25 c.c. or 50 c.c. of the filtered solution (prepared as above described) are measured into a porcelain dish, to which are added 250 c.c. of pure water. To this diluted liquid a solution of $\frac{N}{50}$ permanganate of potash (·632 grm. per litre) is gradually run in from a burette until the liquid, which at first takes a greenish tint, changes to a light yellow. With indigotin and the better qualities of indigo, the end of the reaction is remarkably clear and distinct; and even with an inferior "Kurpah" containing much foreign matter it is easy, with a little practice, to obtain results agreeing very closely with one another.

According to the equation—

$$5C_{16}H_8N_2O_2(HSO_3)_2 + 4KMnO_4 + 6H_2SO_4$$
$$= 5C_{16}H_8N_2O_4(HSO_3)_2 + 2K_2SO_4$$
$$+ 4MnSO_4 + 6H_2O$$
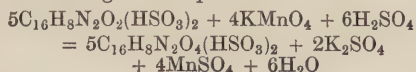
four molecules of potassium permanganate oxidise five molecules of sulphindigotic acid, and consequently 316 parts of potassium permanganate are equivalent to 655 parts of indigotin. Although with a strong solution of indigotin the theoretical quantity of permanganate is decolourised, yet it has been found, on working with a dilute solution, that the end of the titration is reached by the consumption of a smaller amount of potassium permanganate than is indicated by the above equation. In order to obtain comparative results, it is necessary that the solution of indigo should be dilute, in which case the reaction which takes place is not strictly according to the above equation; therefore the strength of the "permanganate" solution should be ascertained by dissolving ·5 grm. of pure indigotin in sulphuric acid and treating the solution obtained as previously described. With the dilution given above, each c.c. of $\frac{N}{50}$ potassium permanganate corresponds to 0·0015 of indigotin.

With pure indigotin dissolved in sulphuric acid, the action of permanganate is strictly quantitative. The end reaction is clearly defined. Different observers with very little practice obtain precisely the same results. Unfortunately, natural indigo usually contains various other substances which more or less act upon permanganate, but the effect of these substances on the results has been much overrated. If the solutions are sufficiently dilute, and care is taken with the titration, fairly accurate results for commercial purposes are obtained with most classes of indigo. If the indigo contains more than 1 or 2 per cent. of indirubin, the end reaction, instead of being yellow, is orange or scarlet, according to the amount of red colouring matter present. When such is the case, the indigotin and indirubin must be estimated gravimetrically, or by one of the methods described on p. 194.

Example.—(1 c.c. of potassium permanganate = ·0015 grm. of indigotin). 1 grm. of "Kurpah" indigo was dissolved in sulphuric acid, diluted to a litre and filtered; 25 c.c. (= ·025 of indigo) diluted with 250 c.c. of water required 8·3 c.c. of permanganate;

$$\therefore \frac{·0015 \times 8·3 \times 100}{·025} = 49·80\% \text{ of indigotin.}$$

If the permanganate solution be strictly $\frac{N}{50}$ and the above quantities be adhered to, it is merely necessary to multiply the number of c.c. of permanganate consumed by 6.

Improved Permanganate Method.—In order to eliminate the error due to the oxidising action of permanganate upon substances other

than indigotin, the colouring matter is pre-
cipitated by common salt, and the extraneous
matter removed by filtration.   The 50 c.c. of
the filtered solution of indigo, instead of being
directly titrated with permanganate, are
mixed in a small flask or bottle with 50 c.c.
of water and 32 grms. of common salt.   The
liquid, which is thus almost saturated with
salt, is allowed to stand for an hour, when it
is filtered and the precipitate washed with
about 50 c.c. of a solution of salt (sp. gr. 1·2).
The precipitated sulphindigotate of soda is
dissolved in hot water, the solution cooled,
mixed with 1 c.c. of sulphuric acid, and
diluted to 300 c.c.   The liquid is then titrated
with potassium permanganate as before.   It
is necessary to make a slight correction in
order to allow for the small quantity of
sodium sulphindigotate which dissolves in a
saturated solution of common salt.   The cor-
rection for the quantities given has been found
to be ·001 grm.   If the indigo, previous to its
solution in sulphuric acid, is treated with
strong hydrochloric acid, washed well with
water and dried, it is unnecessary to precipi-
tate the colouring matter with salt.

Example.—50 c.c. (= ·05 grm. of indigo)
of a 1 grm. per litre solution were mixed
with 50 c.c. of water and 32 grms. of com-
mon salt.   The precipitate was collected
on a filter and dissolved in 300 c.c. of water
containing 1 c.c. of sulphuric acid.   This
solution required 15·2 c.c. of permanganate ;

$$\therefore \frac{(\cdot 0015 \times 15 \cdot 2 + \cdot 001) \times 100}{\cdot 05} = 47 \cdot 60 \,°/_\circ \text{ of indigotin.}$$

Barium Chloride Precipitation Process. *—
It has already been mentioned that the sul-
phuric acid solution of indigo, after making
up to a given volume, must be filtered before
being titrated.   The first portions coming
through the filter are rejected, as filter paper
absorbs some of the colouring matter.   Some
qualities of filter paper absorb more than
others, and the rate of filtration also causes
a difference.   Moreover, some of the sus-
pended impurities are in an exceedingly
fine state of division, and are liable to pass
through many kinds of filter paper, and
thus occasion inaccurate results.

The suspended particles subside after long
standing, but with some classes of indigo
subsidence is not complete after many hours.
Various precipitants were tried, and barium
chloride was found to give the most satisfac-
tory results.   The proportions recommended
are as follows :—0·5 grm. indigo is dissolved
in sulphuric acid as already described, and,
after diluting with water but before making
up to 500 c.c., 10 c.c. of a 20 per cent. solu-
tion of barium chloride are added.   The

solution is poured into a bottle, and the
barium sulphate formed immediately begins
to subside and carries down with it the sus-
pended impurities of the indigo.   In fifteen
to twenty minutes the requisite amount of
perfectly clear solution may be withdrawn by
a pipette for titration.   By this means not
only are the results more concordant but the
solution is clearer than when filter paper is
used.   In fact, the results thus obtained are
practically the same as those given by "salting
out."   Tests made with pure indigotin show
that no colouring matter is precipitated by
the barium chloride.

Donath and Strasser * remove the impuri-
ties by means of various solvents in a Soxhlet's
apparatus as follows :—1 grm. of the finely-
ground indigo is weighed out in a weighing
flask and mixed with four times its volume of
moderately fine dry pumicestone sand.   This
mixture is then placed in a spacious Soxhlet
extractor, on the bottom of which is firmly
secured a layer of asbestos fibre reaching
above the opening of the lateral syphon,
and covered with a thin layer of pumicestone
sand.   The weighing flask after being emptied
into the extractor is also rinsed with pumice-
stone sand.   The indigo is then extracted
with water and hydrochloric acid, a small
quantity of the latter being added through
the condenser as soon as a sufficient quantity
of water has accumulated in the extractor.
The extraction of the glutinous matters is
complete after fifteen minutes' boiling, and
the indigo is then washed with hot water,
which is poured direct into the extractor.
The extractor is then adjusted to the neck of
a flask half-filled with a mixture of four parts
of alcohol and one part of ether, and with
this mixture the indigo is extracted until the
brownish-red colour of the indigo-red has
altogether disappeared, the liquid running
from the extractor being perfectly colourless,
or, at most, only exhibiting a faint blue
coloration.

The extractor, with contents, is now com-
pletely dried at from 100° to 110° C.   The
delivery end of the syphon of the extractor is
then closed with an asbestos plug, the con-
tents of the extractor are completely covered
with concentrated sulphuric acid, and the
extractor, by means of copper wires, is now
suspended in an air bath.   This air bath
consists of a copper cylinder, closed at the
bottom and placed on a tripod.   After heating
the apparatus for from one and a-half to two
hours to 80° C. the sulphonation of the indigo
may be relied upon as complete.   The extrac-
tor is then left to cool ; subsequently the
plug is removed from the syphon and distilled
water poured in.   The indigo-sulphonic acid
formed is thus syphoned off and collected in

* Rawson, *Journ. Soc. Chem. Industry*, 1899, p. 251.

* *Zeit. f. ang. Chem.*, 1894, p. 49 (abs. *Journ. Soc.
Chem. Industry*, 1894, p. 426).

a litre flask, the last traces of dye may be removed from the asbestos by washing with boiling water. The contents of the litre flask are allowed to cool, and the whole is then made up to 1000 c.c. ; 100 c.c. of this solution are diluted with 400 c.c. of water and titrated with a solution of permanganate of potash.

Monosulphonic Acid Method. — Gerland[*] prepares a pure sulphonic acid by previously converting the indigotin into monosulphonic acid, which, on dilution with water, is entirely precipitated. In the first place, he partially purifies the indigo (0·5 grm.) by treating it with hydrogen peroxide and hydrochloric acid, digesting some time in the cold, boiling, filtering, and washing. After drying, it is digested with 40 c.c. of sulphuric acid of specific gravity 1·67 for an hour in the boiling water-bath with repeated shaking. The large excess of sulphuric acid assists the subsequent filtration over the sand filter, which, with less sulphuric acid, would require to be steam-jacketed. Filtration is easily accomplished with a vacuum filter, and washing is performed with acids of the same strength heated to 100°. With proper manipulation the exhaustion of the filter is accomplished with about 40 c.c. more of the acid when the washings have become colourless.

The filtrate is mixed with twice or thrice its own volume of water and filtered. This filtrate is pale yellow, or, with indigo prepared as subsequently described, quite colourless, without a trace of blue in it. The monosulphonic acid remaining on the filter is washed with water containing 20 per cent. of sulphur trioxide. Boiling water dissolves this indigo-sulphonic acid only partially, leaving a small amount of indigo or indigotin compound undissolved. For this reason it is preferable to carry out this operation on a sand filter, dry the whole in an oven, add strong sulphuric acid, digest at about 100° for some time, and remove the indigo, which is now entirely changed into the indigo-disulphonic acid, from the filter by water. An aliquot part of the filtrate is then submitted to titration.

Gerland titrates the solution with a standard solution of "hydrosulphite" or hyposulphite. He uses the apparatus described by Tiemann and Preuss[†] for the estimation of oxygen in water, and adopted by Bernthsen for titration of indigotin.

(b) Hyposulphite Method. — This process, which was recommended by A. Müller,[‡] depends upon the fact that a solution of sodium hyposulphite ($NaHSO_2$) reduces sulphindi-

gotic acid quantitatively to disulpho-leukindigotic acid. The apparatus required for this operation is rather elaborate, and considerable care must be exercised in its manipulation; but when all the details are carried out, analyses may be performed in a short space of time, with very great accuracy.

The mode of procedure given in the following differs somewhat from Müller's description, but only in a few details :—

Preparation of Sodium Hyposulphite. — 100 c.c. of sodium bisulphite ($NaHSO_3$) solution (sp. gr. 1·30) are mixed with 10 grms. of zinc powder in a flask closed by a cork. The flask is immersed in cold water and allowed to stand for about half an hour, when the solution will be found to have lost the smell of sulphurous acid. The liquid is now decoloured, and well mixed in a large flask or bottle, with five litres of distilled water, containing in suspension about 50 grms. of recently slaked lime. The vessel is closed to prevent access of air, and, after allowing the insoluble matters to subside, the clear liquid is syphoned off into a convenient store bottle, and about 100 c.c. of petroleum oil are poured on the surface of the liquid to prevent oxidation. The bottle is provided with a cork through which pass two tubes, one of which is in the form of a syphon, and is used to fill the burette ; the other tube, which only just passes through the cork, is connected with a supply of hydrogen or coal-gas.

Standardising the Hyposulphite. — The solution may be standardised either by pure indigotin, or by an ammoniacal solution of sulphate of copper, using in the latter case a solution of indigo carmine as an indicator. Bernthsen pointed out in 1881[*] that ammoniacal sulphate of copper alone could not be used for estimating the strength of a solution of sodium hyposulphite, as the solution of sulphate of copper became colourless before it was completely reduced. On this account he proposed that, towards the end of the titration, a few drops of indigo-sulphate solution should be added, by which modification the termination of the reaction could be easily and accurately ascertained. Müller found in his experiments that one molecule of ammoniacal sulphate of copper was decoloured by the same quantity of "hyposulphite," as one molecule of indigotin dissolved in sulphuric acid. The standard solution of copper sulphate is prepared by dissolving 1·904 grm. (equal to 1 grm. indigotin) of the crystallised salt ($CuSO_4 . 5H_2O$) in a litre of water containing 100 c.c. of strong ammonia (sp. gr. ·880) ; 50 c.c. of this solution are measured into a wide-mouthed flask (capacity 200 c.c.), boiled to expel air, and allowed to cool. The flask is provided with a caoutchouc stopper,

* *Journ. Soc. Chem. Industry*, 1896, p. 15.
† *Berichte*, vol. xii., p. 1768.
‡ *Berl. Berichte*, vol. xiii., p. 2283, and *American Chemist*, vol v., p. 128.

* *Chemical News*, vol. xliii., p. 79.

perforated with four holes, into two of which are fitted two Mohr's burettes, one containing the hyposulphite solution, and the other the indigo-carmine. The two other apertures serve for the entrance and exit of a current of hydrogen or coal-gas. It is essential that the process should be conducted without access of air. The burette containing the "hyposulphite" is furnished with a perforated cork, through which passes a glass tube connected with a supply of coal-gas; and at the lower extremity a glass tube is joined to it, which is in connection with the bottle filled with sodium hyposulphite above mentioned. By this means the burette can be refilled without fear of oxidising the hyposulphite solution. The flask containing the 50 c.c. of copper sulphate is attached to the caoutchouc stopper, and the air is expelled by a current of coal-gas, which should first pass through U-tubes containing ferrous hydrate. The solution of "hyposulphite" is now gradually run in until the liquid becomes nearly colourless, when a few drops of indigo-carmine are added from the other burette, and finally, a further quantity of hyposulphite is added, until the solution assumes a peculiar brownish-red colour. The end of the reaction is sharp and unmistakable. The quantity of hyposulphite which is used to decolorise the few drops of indigo-carmine solution is very small, but by determining the relative strength of the two liquids, the amount thus consumed can be easily calculated, and then deducted from the number of c.c. used in the titration of the copper sulphate solution. The 50 c.c. of copper sulphate are equivalent to ·05 indigotin, so that supposing 25 c.c. of sodium hyposulphite have been required for the titration, each c.c. of the hyposulphite will correspond to ·002 indigotin. Whenever an analysis of indigo is to be made, the hyposulphite solution requires re-standardising.

Titration of Indigo-Sulphate.—The operation is performed in a similar manner to that just described. 0·5 grm. of finely-powdered indigo is mixed with ground glass, and dissolved in sulphuric acid as previously stated in detail. The sulphindigotic acid is diluted to 500 c.c. and filtered; 50 c.c. of the filtrate are measured into a flask, boiled to expel air, and allowed to cool. The flask is then attached to the burettes, and after driving out the air by a current of coal-gas the "hyposulphite" solution is gradually added, during constant agitation. With indigotin and the better qualities of indigo, the liquid, when fully reduced, becomes of a pale yellow tint, but with inferior samples the solution is more or less of a dirty brownish-yellow colour. In both cases, however, the end of the reaction is quite clear and distinct.

The hyposulphite method gives the percentage of indigotin, and does not include indigo-red.

Example.—50 c.c. standard ammoniacal sulphate of copper (= ·05 indigotin) required 30 c.c. sodium hyposulphite; therefore

$$1 \text{ cc. hyposulphite} = \frac{·05}{30} = ·00166 \text{ indigotin.}$$

1 grm. of Java indigo was dissolved in sulphuric acid, and diluted with water to 1 litre; 50 c.c. (= ·05 indigo) required 20·6 c.c. hyposulphite; therefore

$$\frac{·00166 \times 20·6 \times 100}{·05} = 68·4 \text{ %}_0 \text{ indigotin.}$$

VANADIUM PROCESS. — Engel [*] estimates indigotin by means of a standard vanadium solution. The process is carried out in the following manner:—Vanadic acid, obtained by calcining ammonium vanadate, is treated with zinc and sulphuric acid. A bluish-violet solution of vanadyl sulphate is thus obtained, which, when diluted with water, is found to be capable of reducing and decolourising the blue soluble indigo derivatives. The solution will keep for any length of time. By means of a solution of 1 grm. indigotin in sulphuric acid diluted to 1 litre, a normal solution is obtained containing 0·001 grm. indigo per c.c. The vanadium solution is standarised in such a manner that 1 c.c. will just decolourise 1 c.c. of the indigo solution, and the percentage can thus be obtained directly by reading the number of c.c.s employed. The indigo reduced in this manner rapidly turns blue in contact with the air, and this is liable to render the end reaction indistinct. In order to avoid this, the titration is best effected in a closed flask in an atmosphere of carbonic acid. The commercial vanadate is sufficiently pure to serve for the preparation of the normal solution. For the latter the author dissolves 5 grms. vanadic acid in 25 grms. sulphuric acid with the aid of heat, dilutes the solution to 1 litre and reduces at a temperature not exceeding 50° with 50 grms. zinc. The solution is then filtered and diluted with water as required.

REDUCTION OF INDIGOTIN IN ALKALINE SOLUTIONS.—Numerous processes have been proposed for estimating indigotin gravimetrically by means of reducing agents. They have all one end in view—viz., the formation of indigo-white by the action of nascent hydrogen and its subsequent re-oxidation to indigotin. The separation of the indigotin from the other matters present in indigo by processes of reduction, although a long and tedious operation, is generally considered to give accurate and reliable results. Some of the processes, however, are far from trustworthy. A com-

* *Chem. Zeit.*, 1895, No. 46.

mon method consists of treating finely-powdered indigo, out of contact with air, with a solution of ferrous sulphate and slaked lime. After gently heating the mixture for some hours, the precipitated matters are allowed to subside; a measured volume of the clear liquid is decanted into a beaker, acidulated and oxidised to indigotin. The precipitate is collected on a weighed filter, washed, dried, and weighed. The results obtained by this process are generally too low, as some of the indigotin is thrown down in the reducing flask with the mixed precipitate of iron oxides and lime. Sodium hydrate, as recommended by Crace Calvert, may be used in place of lime.

Reduction by Sodium Hyposulphite and Lime.—The following process, devised by Rawson, gives accurate results, and the percentage of indigotin and indirubin may be obtained separately:—1 grm. of finely-powdered indigo is ground into a thin paste with water and introduced into a flask (cap. about 1500 c.c.) with 500 to 600 c.c. of lime-water. The flask is furnished with an india-rubber stopper, which has three perforations, in one of which is inserted a syphon closed by a pinchcock, while in another is fixed a funnel provided with a stopcock. The third aperture serves, by means of a short bent glass tube, for the entrance of a current of hydrogen or coal-gas. The flask is connected with the gas supply, and the contents heated to about 80°C. About 250 c.c. of a solution of sodium hyposulphite ($NaHSO_2$), about four times as strong as that described on p. 189, are now introduced by means of the funnel, and the mixture, which in a few minutes assumes a yellow tint, is kept near the boiling point for half an hour. After allowing the insoluble matters in the flask to subside, 500 c.c. are syphoned off and the rest of the liquid accurately measured. The 500 c.c. are poured into a conical flask, and, by means of an aspirator, a current of air is drawn through the liquid for about twenty minutes. The excess of hyposulphite is thus oxidised to sulphite, and the indigo-white to indigotin. Hydrochloric acid is then added to dissolve any carbonate of lime which may have been formed, and the precipitate is collected upon a previously dried (105°C.) and weighed filter, washed thoroughly with hot water, dried at 105° C., and weighed. The precipitate thus obtained consists of indigotin and indirubin. In order to determine the amount of each of these constituents, the filter with its contents is placed in an extraction apparatus, and the indirubin dissolved by means of alcohol. The alcoholic solution is allowed to cool, in order that any indigotin may be deposited, after which it is filtered, evaporated to dryness on the water-bath, dried at 105° C., and weighed. The difference between the two weighings

gives the amount of indigotin present, from which the percentage may be easily calculated.

Although, with due care, the precipitated indigotin and indirubin may be obtained free from impurities, with certain low classes of indigo, the product is likely to be contaminated with a little brown matter. When indigotin and indirubin are estimated separately, the error falls on the indirubin. The error may be avoided by dissolving the dry alcoholic extract in concentrated sulphuric acid, diluting with water and very slowly and carefully titrating the filtered solution with $\frac{N}{50}$ permanganate. Or, an aliquot part of the whole precipitate may be dissolved in sulphuric acid, diluted to a given bulk, and a portion titrated with permanganate.

Instead of collecting the regenerated indigo on a weighed filter, it may be run on to an asbestos filter, washed, transferred to a dish and dried; afterwards dissolved in sulphuric acid, diluted with water, and an aliquot part tested by the permanganate method.

In the *Journal of the American Chemical Society* [*] (1885, p. 16), H. M. Rau describes a modification of Fritzsche's method for the analysis of indigo. From 1·5 to 2 grms. of the sample in fine powder are introduced into an 8-oz. Erlenmeyer flask, fitted with a doubly-perforated rubber stopper, through which pass a bent tube provided with a stopcock and reaching just below the stopper, and a second tube of syphon shape reaching nearly to the bottom of the flask. The latter tube terminates in a small funnel, in which a wad of glass wool is placed. From 3 to 4 grms. of pure grape sugar, 15 to 20 c.c. of a 40 per cent. solution of caustic soda, 60 c.c. of water, and about 120 c.c. of 90 per cent. alcohol are added, and the weight of the whole taken. The flask and tubes having been previously weighed alone, a small piece of rubber tubing, closed with a pinch-cock, is slipped over the syphon tube, and the flask heated on the water bath for about half an hour. The reduced indigo readily dissolves, the liquid assuming a deep yellow colour. After about an hour the flask is connected with an apparatus generating carbon dioxide, and the liquid syphoned off as far as possible, the wad of glass wool retaining the solid particles. The flask is again weighed, whereby the weight of the liquid run off is obtained. A current of carbon dioxide is passed through the liquid for about fifteen minutes, and afterwards a current of air, which completes the precipitation. The precipitate is collected upon a dry (110° C.) previously-tared filter, washed with hot dilute hydrochloric acid, and then with boiling water, dried at 110° C., and weighed. The indigotin may be esti-

* Also *Chem. News*, vol. li., 1885, p. 207.

mated with great accuracy by this process, but the indirubin remains in solution unless the liquid is largely diluted with water.

F. A. Owen [*] reduces the indigo by a mixture of zinc dust and strong ammonia, re-oxidises an aliquot portion of the solution, and weighs the washed and dried precipitate of indigotin on a tared filter.

SUBLIMATION.—According to Crum, indigo-blue volatilises in open vessels at about 288° in dark purple-red vapours ; in closed vessels it decomposes partially when heated. According to Dumas, it volatilises without decomposition only in a current of air, or *in vacuo ;* the powder, dropped on a piece of heated platinum foil, volatilises in purple vapours, without leaving a residue, each particle being supported by the vapour, without coming in contact with the foil.

C. T. Lee[†] has employed a method of sublimation for several years which, in his hands, has yielded most satisfactory results. He uses for this purpose shallow platinum trays, 7 cm. long, 2 cm. wide, and 3 to 4 mm. deep. About ·25 grm. of finely-powdered indigo, which has been previously dried at 100°, is weighed into the tray and spread in an even layer over its surface. The operation is conducted on an iron plate, which is heated gradually to avoid burning. When the surface of the indigo is covered with a shining mass of crystals, a piece of sheet iron, bent into the form of a low flat arch, is placed over the platinum tray, and, at the same time, as the temperature rapidly rises, the gas is turned down. The vapours of indigotin are now given off, and the heat is gradually raised ; but care must be taken, lest any yellowish vapours appear, which would indicate the formation of bodies other than indigotin. When all the crystals of indigotin have disappeared from the surface of the residue, the tray with its contents is cooled in a desiccator and weighed. The loss in weight is indigotin. Lee finds that the time for a 50 per cent. indigo is thirty to forty minutes, but soft Java indigo sometimes requires two hours. He also adds that results obtained by this method are constant within ·25 per cent., but frequently he has made re-determinations with variations of only half that error.

At first sight this method appears remarkably simple, combining accuracy with a fair degree of quickness. Indigo, however, contains a variety of substances whose properties have not as yet been thoroughly investigated. But it has been found that indigo-gluten (including other substances soluble in dilute acid), indigo-brown, and indigo-red are all more or less affected by this process of sublimation, and, furthermore, that pure indigo (prepared either by Fritzsche's method or by crystallisation from aniline) is partially decomposed, and leaves a dark brown residue, amounting to upwards of 10 per cent., varying in quantity according to the physical condition of the indigotin operated upon, and also according to the length of time required for the operation. As a rule, inferior qualities of indigo, containing much matter soluble in hydrochloric acid, yield results by this process which are too high ; whilst, on the other hand, indigoes rich in indigotin give results which undoubtedly are too low. When performed under the same arched cover, a given sample of indigo has yielded almost identical results, but when the two analyses have been made under different covers, a difference of upwards of 2 per cent. in the same sample has been usually obtained. The estimation of indigotin by sublimation involves a determination of water in the sample. The principle of the process is a good one, and no doubt further research would yield fruitful results.

EXTRACTION BY VOLATILE SOLVENTS.—A great number of processes have been devised for estimating indigotin in indigo by means of various volatile solvents.

By Aniline.—M. Hoenig [*] recommends the following process :—From ·5 to ·8 grm. of indigo is mixed with about 2·5 grms. of finely-powdered dry pumicestone, and the mixture introduced into a Zulkowsky-Wolfbauer extraction apparatus. About 50 c.c. of aniline or nitrobenzol (preferably the former) are used for extracting. The operation is said to be completed in an hour, but it is recommended that the mass be removed from the apparatus, washed with alcohol, dried, powdered, and extracted a second time. The solution is afterwards evaporated down to a few c.c. and mixed with five times its volume of absolute alcohol. The precipitated indigotin is collected on a weighed filter, washed with alcohol, dried at 110° C., and weighed. There are several objections to this process. Indigotin is by no means readily extracted by aniline ; moreover, the brown impurities are somewhat soluble. Indirubin is not determined since it is removed by the washing with alcohol.

Brandt[†] also recommends the use of aniline oil, and claims an advantage, inasmuch as he removes the excess of aniline by hydrochloric acid instead of alcohol.

By Phenol.—In a later paper[‡] Brandt points out that if the extraction with aniline

[*] *Journ. of Amer. Chem. Soc.,* Nov., 1888 ; *Chem. News,* vol. lxiii., p. 301.

[†] *Chem. News,* Aug., 1884 ; an abstract from the *Journ. of Amer. Chem. Soc.*

[*] *Zeitschr. f. Angew. Chem.,* 1889, No. 10 ; *Analyst,* 1889, p. 177.

[†] *Rev. Gen. des Mat. Colorantes,* 1897, No. 2.

[‡] *Rev. Gen. des Mat. Colorantes,* 1898, p. 26 ; *Journ. Soc. Dyers and Col.,* 1898, p. 34.

is continued beyond a certain time, indigo is rapidly destroyed. In place of aniline he proposes to use phenol, and gives the following directions :—30 grms. of phenol are taken for about 0·2 grm. indigo. The boiling phenol dissolves the indigotin very rapidly, the extraction being complete in less than half an hour. On cooling, the indigo is precipitated in an amorphous state. 20 grms. solid caustic soda dissolved in about 250 c.c. distilled water are now added to the extract and the contents of the vessel shaken. The solution is then filtered through a tared filter, the precipitate washed with boiling water until the filtrate is neutral, then with alcohol until it passes through colourless, or just tinged blue. The precipitate is dried at 110° C. until a constant weight is obtained.

By Naphthalene.—Schneider * recommends the use of naphthalene, and gives the following details of the process :—

The naphthalene (50 grms.) is boiled in an Erlenmeyer flask, through the cork of which passes a tube 15 millimetres in width and a metre long. In the side of the tube within the flask there is an opening, and the bottom of the tube is contracted and slightly bent. The indigo (·5 to 1 grm.) is mixed with glass wool, placed in a paper coil surrounded by a linen one, and suspended below the bottom of the tube in the flask, so that the naphthalene falls into the coil. The boiling must be continued until the drops falling from the coil are quite colourless. On cooling, the naphthalene solution of indigotin is decomposed with ether, filtered, and weighed, as in Stein's method. The correction to be applied for the indigo decomposed and remaining in solution depends on the relative quantities of naphthalene and indigo used, on the duration of the extraction (with 1 grm. of indigo usually 5½ hours), on the manner of heating, and on the possibility of overheating. In order to determine it, the indigotin obtained on the filter should again be extracted with naphthaline under exactly similar conditions, and the loss on again weighing the indigotin gives the necessary correction. With 50 grms. of commercial white naphthalene, which was not quite pure, the loss of indigotin on heating over wire gauze was 1 to 4 milligrammes, corresponding to a correction of + 0·1 to 0·4 per cent., with 1 grm. of indigo. By using purified naphthalene and heating in an oil bath, the loss would certainly have been less.

Care must be taken to have the apparatus and the indigo completely dry, in order to avoid the danger of explosion.

By Nitrobenzol. — Gerland * has made a study of nitrobenzol as applied to the estima-

tion of indigotin in indigo, and has devised a neat and convenient extraction apparatus for the purpose.

The apparatus consists of a large test tube 40 mm. diameter and 15 to 20 cm. long, clamped in a retort stand above a burner ; a brass tube of 7 to 8 mm. inside diameter and about 50 cm. long serves as a reflux condenser. Its lower end is cut obliquely, and has knobs fused to it to secure the wire hook, on which is suspended the filtering tube. This tube is formed of thin glass tubing about 20 mm. diameter and 4 to 4·5 cm. long, both ends slightly enlarged. Over the lower one a piece of fine calico is wired, upon which a few drops of fine paper pulp are placed, this, after drying, forming a serviceable filter. The cloth is protected against the splashings of the boiling nitrobenzol by a small shield, such as the lid of a porcelain crucible. The upper end is tied with thin wire, which allows it to be connected to the hook of the condensing tube. The latter passes through a glass funnel, the stem of which has been cut off, resting on the top of the test tube. The condensing tube is held in a central position in the test tube by means of a cork, through which it passes loosely, so as to allow it to slide up and down, and which is held in a clamp. Lastly, the condensing tube is connected with an aspirator drawing a gentle current of air through the apparatus during the operation.

The ground sample of indigo is weighed into the filtering tube ; this is hooked to the condensing tube, and the latter fastened in its position centrally to the large test tube, so that the filter is about 6 cm. above the bottom of the test tube. The latter is charged with about 25 c.c. of nitrobenzol, the lamp is lighted, and the aspirator set to work. The use of the latter is highly essential to the success of the operation. It draws off the vapours of the boiling nitrobenzol, which would otherwise condense on the sides of the test tube, and escape between its mouth and the covering funnel, and conveys the condensed liquor into the filtering tube. It also carries off the steam from the water, which otherwise would condense and fall into the filter tube, causing explosions. By a careful regulation of the aspirator and the heat, no nitrobenzol vapours escape into the room, and the test tube is fully supplied with condensed liquor. The vapours of the nitrobenzol do not rise in the tube above 20 cm. With 0·5 grm. of indigo and 25 cm. of nitrobenzol, the extraction requires from one-half to one hour, during which time the aspirator discharges about 2 litres of water. Crystals separate at an early stage, but with regular boiling the operation is not interfered with by bumping. When the droppings from the filter tube are colourless

* *Zeit. Anal Chem.*, 1895 ; *Journ. Soc. Dyers and Col.*, 1895, p. 194.

+ *Journ. Soc. Chem. Industry*, 1896, p. 17 ; 1897, p. 108.

the extraction is complete ; the lamp is removed and the apparatus cooled and dismounted. The indigotin separates in beautiful crystals in a deeply-coloured liquor, and only a very small portion remains in solution. To save the trouble of recovering this, nitrobenzol saturated with indigotin in the cold is used. The liquor is passed through an extracted weighed filter, washed with benzol, and dried. The beautiful appearance of the indigotin thus separated is deceptive. It still contains impurity amounting to from 3 to 6 per cent., and is not fit to be tested by the Bernthsen method, owing to the deep coloration. A prolonged treatment with hydrochloric acid, or, better still, with hydrochloric acid and hydrogen peroxide, leaves it in a pure state fit for weighing or testing with hydrosulphite.

By Acetic Acid. — Brylinski * estimates indigotin by means of boiling glacial acetic acid. The indigo to be examined (about 0·15 grm.) is placed in a thimble filter, the diameter of which is slightly larger than that of the Soxhlet flask, in which the extraction takes place. The best results are obtained by pushing the filter into the extraction tube, not to the bottom, but so that it sticks near the top. A plain tube or air condenser is employed, and the boiling of the acetic acid is effected as briskly as possible by means of a free flame. The extraction is continued until the acetic acid passes through colourless.

After the extraction is completed the flask is allowed to cool, and the contents are poured into a beaker and diluted with four times their volume of water. If a small quantity of indigo should remain attached to the walls of the flask, it is dissolved in boiling acetic acid, precipitated with water, and added to the original precipitate. On allowing the liquid to stand for a few minutes, the precipitate collects in flakes. It is filtered on a tared filter, washed, first with boiling water, then with alcohol and with ether, and is finally dried at 110° C. and weighed. Careful washing with alcohol and ether is indispensable, since the acetic acid extracts from the corks and from the filter paper (or from the sample) a substance which is partially precipitated by water, but is soluble in alcohol and in ether.

Other Methods. — F. Voeller † analyses indigo by estimating the nitrogen which a weighed sample contains after purification. The indigo is placed in a perforated platinum crucible closed with asbestos, and with the aid of a filter pump washed successively with hydrochloric acid, soda, alcohol, and hot water. The nitrogen in the residue is then estimated by Kjeldahl's method, and the percentage found multiplied by the factor 9·36 gives the indigotin. An analysis of commercial indigo quoted by Voeller gave 75·76 per cent. of indigotin, 16·35 per cent. of mineral matter, and 6·48 per cent. of water. But commercial indigo containing so much mineral matter and water *never* contains such a high percentage of indigotin. Presuming the method to give accurate results, it would be altogether unsuitable for commercial purposes. Furthermore, the indirubin is removed by washing with alcohol.

DYE TESTS.—Grossmann, in a paper published in the *Journal of the Society of Dyers and Colourists*, 1897, p. 124, gives a general review of the principal methods published up to that date. He gives a description of a method of testing indigo by means of dye-trials. The indigo to be tested is purified and converted into the soluble sulphonic acid compound, and a special form of apparatus is used.

INDIGO RICH IN INDIRUBIN.—A considerable amount of indigo now on the market contains a large proportion of indirubin. *

With indigo containing more than 1 or 2 per cent. of indirubin, the ordinary methods of analysis suitable for estimating indigotin are not applicable. The gravimetric hyposulphite method may be used, but for commercial purposes this is rather a lengthy operation. Very good results may be obtained by a colorimetric method. For this purpose the following is recommended :— From 0·1 to 0·25 grm. of the finely-powdered sample is boiled with about 150 c.c. of ether for half an hour in a flask attached to an inverted condenser. When cold, the solution is made up to 200 c.c. with ether and mixed with 10 c.c. of water in a bottle. Shaking up with a little water causes the suspended particles of indigo to settle immediately, and a clear solution of indirubin is at once obtained without filtering. A measured quantity of the solution is withdrawn and compared in a colorimeter with a standard solution of indirubin. The proportion of ether recommended may seem large, but although pure indirubin is freely soluble in ether, it is by no means readily extracted from indigo.

For the estimation of indigotin in indigo rich in indirubin, it is advisable to boil up repeatedly with alcohol, and collect the residue on an asbestos filter, wash, dry, dissolve in sulphuric acid, dilute with addition of barium chloride, and titrate an aliquot part of the clear solution with permanganate.

Koppeschaar † determines the indigotin and indirubin colorimetrically, separating the two colouring matters by means of acetic acid, as

* *Rev. gen. des Mat. Colorantes*, 1898, p. 52 : *Journ. Soc. Dyers and Col.*, 1898, p. 75.
† *Zeitschr. f. angew. Chem.* 1891, p. 110 ; *Journ. Soc. Chem. Ind.*, 1891, p. 488.

* *Journ. Soc. Chem. Ind.*, 1899, p. 252.
† *Zeit. fur. Anal. Chem.*, 1899, p. 1.

follows :—0·5 grm. of the finely-powdered sample of indigo is put into an Erlenmeyer flask of 8 to 9 cm. diameter along with 100 c.c. glacial acetic acid; on heating for one hour on a steam bath, the indigo-red passes into solution. The flask is then allowed to cool in an inclined position, so that the liquid reaches the neck, and when the insoluble portion has completely settled, the clear solution is carefully decanted on to a filter. The funnel should have a diameter of 8 cm., and is charged with a little glass wool, then with a few pieces of pumice stone, and, finally, a layer of asbestos well pressed down. The filtration is conducted with much caution, in order to avoid bringing any undissolved indigo on to the filter. If the colour of the filtrate shows that much indigo-red is present, the insoluble portion should be washed with a little more acetic acid, using the same precautions as to subsidence and decantation. The asbestos layer from the filter, which may contain a few particles of the insoluble portion, is then pushed and washed through into the flask with 50 c.c. of pure sulphuric acid, which is then heated for two hours at 70° C. to dissolve the indigo-blue; the solution is subsequently diluted to a definite volume and the amount of indigo-blue determined colorimetrically by comparison with a standard solution prepared from a pure synthetic indigo such as that of the Badische Anilin und Soda Fabrik. This should be heated with glacial acetic acid at 100° C., then filtered and dried, and of this 0·1 grm. is dissolved in sulphuric acid and diluted to one litre.

For the determination of the indigo-red an aliquot part of the acetic acid solution is neutralised with caustic soda lye, using 12 c.c. of 20 per cent. caustic soda solution for every 5 c.c. of the acetic acid solution. The indigo-red which is precipitated is freed from indigo-brown by washing with a 5 per cent. caustic soda lye. The precipitate is then collected on a filter, which is afterwards dried and shaken with glacial acetic acid in a 50 c.c. flask. The solution of indigo-red is made up to the mark with acetic acid, and the determination is made by comparing the colour with a standard solution containing 0·5 grm. pure indigo-red in one litre. The pure indigo-red is prepared by extracting Java indigo with hot glacial acetic acid and diluting the clear solution with water to precipitate the indigo-red, which is then freed from indigo-brown by washing with caustic soda solution. The indigo-red so obtained can be easily purified by sublimation under reduced pressure. If the indigo sample contains more than 10 per cent. of indigo-red, it will be necessary to dilute with an equal volume of glacial acetic acid; if the amount be less than 10 per cent. it will be necessary

to dilute the standard solution in like manner for the purpose of comparison. The possible error in the determination of indigo-blue by the colorimetric method lies between 0·2 and 0·8 per cent.; for indigo-red the error is still less.

YELLOW COLOURING MATTER IN INDIGO. —Several samples of Java indigo have recently been found to contain a yellow substance * which interferes greatly with the ordinary methods of estimating indigotin.

This substance is almost insoluble in water or in dilute acids, but dissolves in concentrated sulphuric acid and remains in solution on dilution with water. On the addition of salt to this solution, a precipitate is obtained which is soluble in water. It is soluble in glacial acetic acid. The compound dissolves readily in alkaline solutions with a deep yellow colour; on the addition of dilute acids it is thrown down as a pale yellow flocculent precipitate. It is soluble in alcohol and ether, forming colourless solutions, but a trace of alkali produces a deep bright yellow. On the application of a gentle heat the substance melts, partially sublimes, gives off dense, yellowish-white vapours, and leaves a mass of carbon. Although nearly insoluble in water it dyes wool mordanted with bichromate of potash a good yellow shade, resembling that given by weld or vine leaves. It does not dye unmordanted wool, hence it is a mordant colour.

Its presence may readily be detected by the addition of a solution of caustic soda or ammonia to the powdered indigo placed in a porcelain basin or on a filter paper. If present, the alkali immediately produces a deep yellow colour. When this occurs the weighed amount of indigo to be tested should be heated, either with a dilute solution of ammonia or with alcohol, and poured on to an asbestos filter, washed and dried, and then dissolved in sulphuric acid for further treatment. Boiling alcohol is preferable for this purpose, since alkaline solutions containing indigo in suspension are difficult to filter, and under certain conditions indigo enters into solution. At the same time indirubin is removed, and that must be taken into account.

Gerland's monosulphonic acid process is not applicable since the yellow body is dissolved by sulphuric acid of sp. gr. 1·67, and is precipitated on dilution with water.

WATER IN INDIGO.—In testing indigo it is very important that the amount of water present should be taken into consideration, although this factor is generally overlooked. Indigo both in lumps and in the powdered state is very liable to change in weight, either drying, or absorbing water from the air, according to the atmospheric conditions. This property is often the cause of apparent

* Rawson, *Journ. Soc. Chem. Ind.*, 1899, p. 251.

discrepancies in testing. A sample of indigo representing a chest or a number of chests may frequently be found to contain 5 per cent. less moisture than the bulk. Afterwards, on delivery of the chests, tests for indigotin are made, and the results naturally come out lower. The indigo is inferred to be of inferior quality, although the difference may be due entirely to a difference in " condition " or amount of moisture present.

In order to show more clearly the possible variations in the percentage of colouring matter in samples presumably the same, a number of indigoes were exposed under different atmospheric conditions. The results are given on the accompanying table. Two samples of Bengal, two of Kurpah, one of West African, and one mixed lot were taken. The experiments were made in two series; series A in lumps and series B in powder.

TABLE SHOWING VARIATION IN WEIGHT OF SAMPLES OF INDIGO EXPOSED UNDER

	Mean Temperature of Air during Exposure.	Humidity of Air. Complete Saturation = 100.	Type of Indigo with Percentage of Indigotin and Indirubin.					
			Bengal, 57·80.		Bengal, 59·50.		Kurpah, 50·40.	
			Weight grms.	Water p. ct.	Weight grms.	Water p. ct.	Weight grms.	Water p. ct.
SERIES A.—INDIGO IN LUMPS.	Deg. F.							
Exposed in room heated by gas-stove. Air moderately still—								
At commencement of experiment,	..	..	200	6·90	200	6·10	200	11·25
After 1 day,	63	63	198·70	6·25	198·85	5·52	196·15	9·33
,, 2 days,	72	50	197·85	5·82	198·35	5·28	193·85	8·17
,, 3 ,,	75	54	196·50	5·15	197·50	4·85	191·35	6·93
,, 4 ,,	76	54	195·85	4·82	197·15	4·67	189·75	6·13
,, 5 ,,	75	51	195·15	4·47	196·65	4·42	188·65	5·57
,, 6 ,,	71	53	194·65	4·32	196·35	4·28	188·10	5·30
,, 7 ,,	72	50	194·55	4·27	196·20	4·20	187·80	5·15
Exposed in cool, damp cellar—								
After 1 day (from previous exper.),	44	100	196·70	5·25	198·20	5·20	190·00	6·25
,, 2 days,	44	100	198·15	5·97	199·55	5·87	191·35	6·92
,, 3 ,,	44	100	199·25	6·52	200·55	6·37	192·35	7·43
,, 4 ,,	45	100	200·35	7·07	201·50	6·85	193·35	7·92
,, 11 ,,	47	100	204·25	9·02	205·75	8·97	198·15	10·32
,, 13 ,,	47	100	204·90	9·35	206·40	9·30	199·05	10·77
Exposed in cupboard in gentle current of air—								
After 1 day (from previous exper.),	85	72	194·15	3·97	196·75	4·47	188·25	5·37
,, 2 days,	85	66	193·25	3·52	194·85	3·52	187·25	4·77
,, 3 ,,	85	66	192·55	3·17	194·05	3·12	186·40	4·45
SERIES B.—INDIGO IN POWDER.								
Exposed in room heated by gas-stove. Air moderately still—								
At commencement of experiment,	..	..	25	6·90	25	6·10	25	11·25
After 1 day,	63	63	24·68	5·62	24·88	5·62	24·08	7·57
,, 2 days,	72	50	24·58	5·22	24·75	5·10	23·68	5·97
,, 3 ,,	75	54	24·43	4·62	24·63	4·62	23·46	5·09
,, 4 ,,	76	54	24·42	4·58	24·62	4·58	23·43	4·97
,, 5 ,,	75	51	24·36	4·34	24·56	4·34	23·38	4·77
,, 6 ,,	71	53	24·35	4·30	24·55	4·30	23·37	4·73
,, 7 ,,	72	50	24·33	4·22	24·53	4·22	23·34	4·61
Exposed in cool, damp cellar—								
After 1 day (from previous exper.),	44	100	24·96	6·74	25·03	6·22	24·00	7·25
,, 2 days,	44	100	25·22	7·78	25·30	7·30	24·33	8·57
,, 3 ,,	44	100	25·41	8·54	25·48	7·82	24·53	9·37
,, 4 ,,	45	100	25·55	9·10	25·63	8·62	24·70	10·05
,, 11 ,,	47	100	26·12	11·38	26·28	11·22	25·33	12·57
,, 13 ,,	47	100	26·18	11·62	26·34	11·46	25·42	13·93
Exposed in cupboard in gentle current of air—								
After 1 day (from previous exper.).	85	72	24·13	3·42	24·48	4·02	23·23	4·17
,, 2 days,	85	66	24·12	3·48	24·40	3·70	23·20	4·05
,, 3 ,,	85	66	24·10	3·44	24·30	3·30	23·13	3·77

In the former case 200 grms. were taken, and in the latter 25 grms. The indigo was kept for a period of seven days in a room with the temperature averaging 72° F. and the humidity 53. The air was moderately still. The samples were then taken into a cool damp cellar, where the temperature averaged 45° to 46° F., and the air was saturated with moisture. They were afterwards exposed in a draught cupboard to a gentle current of air; the temperature was maintained at 85° F. and the humidity averaged 68.

It will be observed that the damp Kurpah, containing originally 11·25 per cent. of water, lost upwards of 6 per cent. in seven days at 72° F. in the lump form. In the powder, a loss of 6 per cent. was observed in three days. At a temperature of 85° F., in a gentle current of air, the loss, as was to be expected, was much more rapid; most of the samples, even

VARIOUS ATMOSPHERIC CONDITIONS AS REGARDS TEMPERATURE AND HUMIDITY.

	Mean Temperature of Air during Exposure.	Humidity of Air. Complete Saturation = 100.	TYPE OF INDIGO WITH PERCENTAGE OF INDIGOTIN AND INDIRUBIN.					
			Kurpah, 41·75.		African, 39·80.		Mixed, 52·85.	
			Weight grms.	Water p. ct.	Weight grms.	Water p. ct.	Weight grms.	Water p. ct.
SERIES A.—INDIGO IN LUMPS.	Deg. F.							
Exposed in room heated by gas-stove. Air moderately still—								
At commencement of experiment,	..	..	200	8·80	200	6·45	200	9·95
After 1 day,	63	63	199·00	8·30	197·90	5·40	197·15	8·52
,, 2 days,	72	50	198·25	7·92	196·65	4·77	195·85	7·87
,, 3 ,,	75	54	197·20	7·40	195·95	4·42	193·80	6·85
,, 4 ,,	76	54	196·80	7·20	195·70	4·30	192·95	6·42
,, 5 ,,	75	51	196·15	6·88	195·35	4·12	192·05	5·97
,, 6 ,,	71	53	195·75	6·67	195·20	4·05	191·75	5·82
,, 7 ,,	72	50	195·50	6·55	195·05	3·97	191·45	5·67
Exposed in cool, damp cellar—								
After 1 day (from previous exper.),	44	100	197·30	7·45	197·15	5·02	193·50	6·70
,, 2 days,	44	100	198·50	8·05	198·10	5·50	194·60	7·25
,, 3 ,,	44	100	199·45	8·52	198·85	5·87	195·55	7·67
,, 4 ,,	45	100	200·45	9·02	199·60	6·25	196·30	8·10
,, 11 ,,	47	100	205·30	11·45	202·30	7·60	199·65	9·77
,, 13 ,,	47	100	206·05	11·82	202·75	7·82	200·25	10·07
Exposed in draught cupboard in gentle current of air—								
After 1 day (from previous exper.),	85	72	196·10	6·85	194·70	3·80	192·25	6·07
,, 2 days,	85	66	193·65	5·62	194·10	3·50	189·75	4·82
,, 3 ,,	85	66	193·35	5·47	193·50	3·20	189·35	4·62
SERIES B.—INDIGO IN POWDER.								
Exposed in room heated by gas-stove. Air moderately still—								
At commencement of experiment,	..	..	25	8·80	25	6·45	25	9·95
After 1 day,	63	63	24·88	8·32	24·70	5·25	24·38	7·47
,, 2 days,	72	50	24·74	7·76	24·60	4·45	24·08	6·27
,, 3 ,,	75	54	24·50	6·80	24·55	4·25	23·88	5·47
,, 4 ,,	76	54	24·49	6·76	24·52	4·13	23·87	5·43
,, 5 ,,	75	51	24·40	6·40	24·47	4·33	23·80	5·15
,, 6 ,,	71	53	24·37	6·28	24·46	4·29	23·78	5·07
,, 7 ,,	72	50	24·36	6·24	24·44	4·21	23·76	4·99
Exposed in cool, damp cellar—								
After 1 day (from previous exper.),	44	100	25·05	9·00	24·97	6·33	24·33	7·27
,, 2 days,	44	100	25·40	11·20	25·20	7·25	24·58	8·27
,, 3 ,,	44	100	25·65	11·40	25·30	7·65	24·73	8·87
,, 4 ,,	45	100	25·85	12·20	25·35	7·85	24·83	9·27
,, 11 ,,	47	100	26·55	15·00	25·70	9·25	25·23	10·87
,, 13 ,,	47	100	26·66	15·44	25·75	9·45	25·33	11·37
Exposed in cupboard in gentle current of air—								
After 1 day (from previous exper.),	85	72	24·60	7·20	24·40	4·05	23·83	5·27
,, 2 days,	85	66	24·34	6·16	24·35	3·85	23·70	4·75
,, 3 ,,	85	66	24·20	5·60	24·25	3·45	23·53	4·07

in the lump form, losing about 6 per cent. in two days. The experiments further show that dry indigo exposed in a cool damp place is capable of absorbing from 4 to 5 per cent. of moisture in the course of about a week.

The amount of water in indigo is readily determined by heating 1 grm. of the powdered sample to a temperature of 105° to 110° C. in an air-oven for about an hour, cooling in the desiccator and re-weighing. For this kind of determination watch-glasses are usually recommended, but when a number of samples are to be tested it is more convenient to use small beakers about an inch high.

ASH OR MINERAL MATTER IN INDIGO.—It is frequently desirable to estimate the amount of ash in indigo. For this purpose 1 grm. is weighed into a platinum capsule or crucible and ignited over a Bunsen burner, fitted with a rose. At first the flame should be very low, just sufficient to volatilise the indigotin, and throughout the whole operation the heat should not be very great. Some samples are very difficult to burn off completely over a Bunsen. It is preferable to use a muffle furnace at a low red heat, when a number of samples are to be operated upon at the same time.

Detection and Estimation of Indigo on the Fibre.

Indigo when present alone on the fibre may be easily identified, but in small quantities, or in the presence of certain other colouring matters, some difficulty is experienced in detecting it. Indigo is a substantive dye, and requires no mordant. Consequently, a pure indigo-dyed cloth should contain no mordant. The presence of chromium oxide in the ash of woollen cloth indicates (but does not prove) the presence of logwood or some other mordant dye. Woollen material dyed with *pure* indigo is not affected by hydrochloric acid, dilute sulphuric acid, soap, alkalies, or cold alcohol. Hot soap solutions and alkalies remove some of the colour from cotton dyed with indigo. Boiling alcohol extracts a small quantity of blue colour, but, on cooling, the minute amount of indigo thus extracted separates and the liquid becomes colourless. Hot solutions of aniline, amylic alcohol, chloroform, and nitrobenzol extract the colouring matter to a greater extent.

When the fibre is treated with cold concentrated sulphuric acid the liquid at first becomes yellow, quickly olive, and slowly changes from green to a deep blue. On the addition of water the solution remains blue ; the fibre (if wool) also is usually of a light blue colour. If the solution is boiled with a piece of white wool, the latter is dyed a bright blue shade similar to indigo extract,

and gives all the reactions of indigo extract. A drop of strong nitric acid gives a yellow spot surrounded by a green rim with indigo-dyed goods. This test is commonly applied by merchants and others to ascertain whether a sample of cloth is dyed with pure indigo or not. The test known as the "nitric acid test" applied alone is of no value whatever, since many other blue colouring matters give practically the same reaction. Some who have discarded the "nitric acid test" apply another, which, however, is also fallacious as a universal test. They immerse the cloth in hot dilute hydrochloric or sulphuric acid, and if it remains blue conclude that it is indigo. As a test to distinguish between indigo and logwood it is quite satisfactory, but a great number of blue colouring matters resist the action of moderately strong acids remarkably well.

Fabrics (especially cotton goods) dyed with indigo, yield purple-coloured vapours of indigotin when gently ignited. If a piece of porcelain or glass be held over the vapours, a blue deposit is obtained. This is not a delicate test, and is of little value when only small quantities of indigo are present on the fibre. If present in compound shades, indigo may usually be detected by boiling two or three times with dilute hydrochloric acid, washing with water, and then boiling with a weak solution (about $\frac{1}{2}$ per cent.) of sodium carbonate. The fibre is then dried and the various tests above mentioned applied. For the detection of very small quantities of indigo in compound shades (blacks, browns, &c.), a solution of sodium hyposulphite, prepared by the action of zinc on sodium bisulphite, is a delicate test. The material is boiled with dilute acids, and, if indigo extract is present, afterwards boiled repeatedly with a $\frac{1}{2}$ per cent. solution of sodium carbonate until the whole of it is removed. The fibre is then warmed gently with a solution of the hyposulphite, and the liquid poured into a dish, or on filter paper. In a few minutes the hyposulphite is oxidised and the reduced indigo (if present) is converted into indigo-blue, which is deposited as a film on the basin or filter paper. The blue precipitate may, if necessary, be collected and further treated.

In order to get a deeper as well as a brighter and redder shade on cotton yarn, after dyeing with indigo, the material is often "topped" with methyl violet or benzidine reds. Methyl violet is detected by boiling with alcohol, allowing the solution to cool, and filtering. The violet solution may be added to water and a small piece of wool dyed in the liquid. The wool is dried and the presence of methyl violet confirmed by special tests. The presence of "benzidine" red is indicated by white cotton becoming dyed red when boiled

in a slightly alkaline solution with the sample of material.

In the *Journal of the Society of Dyers and Colourists*, 1887, pp. 127, 140, 159, 178, a series of tables is given by W. Lenz for detecting various other colours in indigo-dyed goods.

Various methods have been proposed for the *estimation* of indigo in dyed material. For wool and woollen fabrics (in the absence of other colouring matters) good results may be obtained by simply treating with concentrated sulphuric acid, filtering through glass wool, and washing at first with pure sulphuric acid, and finally with water. The solution is made up to a known bulk, and the amount of indigotin present determined colorimetrically. The method is not suitable for cotton goods or mixed fabrics. Indigotin on cotton may be conveniently estimated by means of sodium hyposulphite and lime, as described under *Analysis of Indigo*. In this case the re-generated indigotin should be collected on an asbestos filter, washed, dried, dissolved in concentrated sulphuric acid, and the indigotin determined either colorimetrically or by permanganate. Indigo on dyed material may also be estimated by means of the various volatile solvents described under *Analysis of Indigo*. Gerland strongly recommends the use of nitrobenzol for this purpose, and finds that the extraction takes place much more rapidly if the material is treated in the first place with boiling acetic acid. He prefers, however, to destroy the fibre (wool or cotton) with strong mineral acids before extracting with nitrobenzol. Brylinski recommends the use of acetic acid for extracting indigotin from the fibre (see *Analysis of Indigo*). Binz and Rung [*] also use glacial acetic acid, and slightly modify Brylinski's process.

Indigo Extract.

It has been previously stated that when indigo is treated with concentrated sulphuric acid it dissolves, forming mono- and disulphonic acids. According to the subsequent treatment which the solution receives, the products are known as *chemic, acid or sour extract, neutral or sweet extract, refined extract, indigo - carmine, soluble indigo, &c.* When a moderate proportion of acid is used and allowed to act for a short time only, indigomonosulphonic acid is principally formed. This product converted into its sodium salt forms what is known as *red* or *purple indigo extract*. Its use is somewhat limited ; the disulphonic compounds having a much wider application. For the manufacture of "indigo extract," one part of finely-

* *Zeit. Angew. Chemie.*, 1898, p. 904 ; *Journ. Soc. Dyers and Col.*, 1899, p. 75.

ground dry indigo is slowly mixed with from five to six parts of concentrated sulphuric acid in an earthenware vessel. The best plan is to carefully add the indigo to the sulphuric acid in small portions at a time during constant stirring with a wooden or, preferably, porcelain stirrer. The vessel is then placed in hot water, at a temperature of 50° to 60° C., for about an hour, taking care to stir the mixture occasionally. It will often be found that after well stirring dry little balls of powdered indigo rise to the surface. The mixture is allowed to stand covered up for a period of about twenty-four hours. The product thus obtained is known in the dye-house as *chemic*, or *Saxony blue*. It was formerly used in this state much more than at present; it now usually receives a further treatment. Unless the indigo is of very fine quality, previous to dissolving in sulphuric acid, it should be broken up into small pieces or ground to a coarse powder and treated with strong hydrochloric acid. After standing about a quarter of an hour, hot water is added, and the whole thrown on to a filter, and the mass thoroughly washed with boiling water. The partially purified indigo is then dried, ground, and dissolved in sulphuric acid, as above described. In order to convert the acid solution into "extract" it is diluted with water and treated with a saturated solution of common salt, which precipitates the colouring matter. After standing an hour or two, the mixture is ladled on to a filter made of strong woollen cloth laid upon wooden frames. Between the cloth and the frame cocoa-nut matting or straw is placed, in order to allow the liquid portion to run off more freely. By this operation a great portion of the free acid, as well as a valueless green colouring matter, is removed. The pasty mass on the filter is known as *acid indigo extract*. It is left to drain for a period of from one to ten days, according to the "strength" of extract required and then placed in casks.

Neutral or Sweet Extract of Indigo is obtained in one or two ways. The acid extract may be dissolved in water, reprecipitated by salt, and again filtered. In order to remove the free acid completely the process must be repeated two or three times. The free acid is also removed by neutralising the solution with sodium carbonate, adding salt, and filtering as before. A purer extract is obtained (often known as *refined extract*) by filtering the acid solution of indigo previous to adding sodium carbonate or salt. In this way a considerable amount (varying according to the quality of indigo used) of a dirty green useless colouring matter is removed. The extract may be further purified by dissolving it in water, reprecipitating with salt, and filtering.

A still purer extract is obtained (*best refined*

extract) by treating indigotin or refined indigo with sulphuric acid.

Soluble indigo (*indigo-carmine*) is the best refined extract (neutralised) made from refined indigo, dried, and ground. It should dissolve in water without leaving any residue, and should be free from any green impurities.

Application.—Indigo extract is not applicable to cotton, but is largely used for silk and wool, although it has been to a considerable extent replaced by various kinds of aniline blues. The more acid varieties are employed for dyeing woollen and worsted goods. Neutral extract is employed for silk, and particularly for dyeing the worsted of mixed or union goods. It is also used in printing woollen material and worsted yarn for tapestry carpets, &c. Indigo extract is usually dyed in a bath containing sulphuric acid and sodium sulphate. If the extract is very acid, no further addition is necessary, although within certain limits the more acid the bath is the better is it exhausted. Sodium sulphate is employed in order to obtain more regular dyeing, the colour working on the wool or silk more slowly. In place of sulphuric acid, alum and tartar are sometimes employed.

The shades produced with indigo extract are much brighter than those given by *vat indigo*, but, unfortunately, they are not fast. By conversion into its sulphonic acid derivative, the properties of indigo are entirely changed. Washing with soap and weak alkaline solutions more or less readily removes the colouring matter from the fibre, and, on exposure to light, the shade fades, the time varying, of course, according to its depth of colour and the conditions under which it is exposed.

TESTING OF INDIGO EXTRACT.—The value of indigo extract may be determined by any of the methods described under the heading, "*Conversion into indigo sulphonic acid.*" The barium chloride precipitation method is the most suitable. About 10 grms. of extract are dissolved in a litre of water, and 50 to 100 c.c. of the solution titrated in the presence of sulphuric acid with $\frac{N}{50}$ permanganate, as previously described.

Comparative dye tests are especially valuable for indicating the purity of shade. Samples of extract of indigo vary very much in this respect. The tests are best made on worsted yarn or cloth ; about 5 per cent. of "extract" and 5 per cent. of sulphuric acid are convenient quantities to use. *Refined* indigo extract should dissolve completely in water, leaving no green or greenish-grey residue. Common indigo extract contains more or less dirty green insoluble substances.

Estimation of Free Acid.—There are "acid" indigo extracts and "neutral" indigo extracts,

but the latter, as sold, frequently contain also more or less free acid. The amount of free acid may be readily determined by precipitating the colouring matter with pure salt. For this purpose 100 c.c. of a 1 per cent. solution of the extract is treated with 32 grms. of sodium chloride, and, after standing an hour with occasional shaking, filtered, and the precipitate washed with a little saturated solution of salt. The filtrate, which is slightly coloured (but this does not interfere with the reaction), is titrated with $\frac{N}{10}$ caustic soda and phenolphthalein. With a little practice fairly good results may be obtained by titrating direct, without resorting to precipitation.

ADULTERATION.—Samples of indigo extract frequently contain *soluble blue* and similar coal-tar blues. These may be usually detected by dyeing a skein of silk in an acidified solution of the sample, washing, and boiling in a large volume of fresh water. When the boiling is repeated two or three times, almost the whole of the indigo extract is removed, and the aniline blue remains on the fibre. The presence of soluble blue is also indicated by the action of potassium permanganate on a solution of the sample. With pure indigo extract the solution becomes yellow ; whereas if aniline blue is present, it changes to a lighter blue, violet or grey. After destroying the indigo by permanganate, a small piece of wool or silk may be dyed in the solution, and the colour recognised on the fibre by special tests.

EXTRACT OF INDIGO ON THE FIBRE is distinguished from vat indigo by the colour being removed on boiling with a dilute solution ($\frac{1}{2}$ per cent.) of sodium carbonate. On the addition of an acid to the solution, the colour is intensified, and wool or silk may be dyed blue in it. The acidulated solution is decolorised by potassium permanganate. Strong hydrochloric acid turns the fibre greenish-blue, and caustic soda turns it green. Nitric acid gives a yellow spot, as with vat indigo.

ARTIFICIAL INDIGO EXTRACT.—The *sodium salt of indigotin disulphonic acid* is obtained by the fusion of *phenylglycocol sulphonic acid* with caustic soda, with subsequent oxidation of the product.

INDIGO SALT (K.). 1893. Yellow crystalline mass consisting of the sodium bisulphite compound of *orthonitrophenyl lacto ketone*

$$(C_6H_4\!\!<\!\!{CH(OH) . CH_2 . CO . CH_3 + NaHSO_3) \atop NO_2}),$$
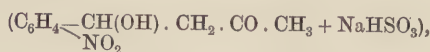
which, on treatment with dilute alkali, is converted into indigotin.

Under the name "indigo salt T," the free ketone is now sold as a buff powder, which is insoluble in water. This product forms the

above soluble compound on treatment with a strong solution of sodium bisulphite. It is used in *calico* printing.

INDIGO BLUE N, SGN (C.). Acid blues for wool.

INDISIN *v.* ROSOLANE.

INDOIN BLUE R (B.) (G.). An azo dye.

Safranine — Beta-naphthol.

1891. Dark coloured paste or bronzy powder, slightly soluble in water with a violet colour. In concentrated H_2SO_4, greenish-brown solution; on dilution, green solution, then violet precipitate.

Application.—A direct and a basic dye. Dyes unmordanted or tannin - mordanted *cotton* indigo-blue. A very fast dye.

INDOLINE (Mo.). A basic navy-blue dye.

INDOL BLUE R (Ber.). A basic navy-blue dye.

INDOPHENINE EXTRA (By.) *v.* INDULINE.

INDOPHENOL (D. & H.). Produced by the action of *nitrosodimethyl aniline* on *alpha-naphthol*. 1881. Dark brown powder, insoluble in water. In concentrated H_2SO_4, yellowish-brown solution; on dilution, brown ppt.

Application.—Used for dyeing *wool* or *cotton* by the vat process. The indophenol, alone or mixed with indigo, is treated with an alkaline reducing agent, which converts it into soluble *Indophenol white*. After saturating the material, the blue is reproduced by exposure to air and by passing through a dilute solution of (*e.g.*) chromic acid.

INDOPHENOL WHITE (D. & H.) (C.). The reduction product of *indophenol*, acetate of tin being the usual reducing agent. Yellow paste, soluble in boiling water.

INDOPHOR. A mixture of *indoxyl* (C_5H_7 . N . O) and *indoxylic acid* (C_5H_6 . N . O . COOH). On steaming, cotton padded with indophor yields indigo. It was introduced in 1895 by B.A.S.F. for use in padding and printing cotton.

Reissert (1896) obtained indigotin by the following process :—

Orthonitro toluidine $\left(C_6H_4\!<\!{{CH_3}\atop{NO_2}}\right)$ is condensed with *oxalic acid*, forming *orthonitrophenyl pyrouvic acid* $\left(C_6H_4\!<\!{{CH_2.CO.COOH}\atop{NO_2}}\right)$. The latter, on reduction with sodium amalgam, forms *oxyindolcarboxylic acid* $\left(C_6H_4\!<\!{{CH}\atop{N(OH)}}\!>\!C . COOH\right)$, and this product, on being allowed to stand in concentrated H_2SO_4, yields indigo on saturation with ammonia and subsequent aeration.

INDULINE (SOLUBLE IN SPIRIT) (B.) (By.) (C.R.) (N.J.) (P.) (S.C.I.). *Fast blue*

spirit soluble (Ber.), *Azine blue spirit soluble* (D.), *Indigen D and F* (By.), *Indophenin extra* (By.), *Blue CB spirit soluble* (D. & H.), *Induline opal*, *Printing blue* (Ber.), *Acetin blue* (B.), *Pelican blue*, *Nigrosin spirit soluble* (B.) (Ber.), *Coupier's blue*, *Sloleine*, *Azo diphenyl blue*, *Violaniline.*

Indulines are prepared by heating *amido-azobenzene* with *aniline* and *aniline hydrochloride.*

Nigrosines are prepared (1) by heating *nitrobenzene* with *aniline*, *aniline hydrochloride*, and *iron*; (2) by heating *nitrophenol* with *aniline* and *aniline hydrochloride.*

The *red shades* are produced at the lower temperatures, the *blue shades* by a more prolonged action at a higher temperature.

The paste or liquid colours are mixed with, or dissolved in, some organic solvent, such as *alcohol, acetic acid, acetin, &c.*

The indulines form bluish-black or brownish - black pastes or powders, insoluble in water. In concentrated H_2SO_4, they usually give a blue solution, which, on dilution, yields a violet-blue ppt.

Application.—Basic dyes. Used to a small extent in *calico* printing, but principally for the preparation of the soluble indulines, and in making black spirit *varnishes.*

INDULINE (SOLUBLE IN WATER). *Induline* (B.) (By.) (C.R.) (N.J.) (D.), *Induline R and B* (K.), *Fast blue 3 R, R and B* (Ber.) (M.) (B.) (C.), *Fast blue 6 B* (Ber.), *Fast blue-greenish* (B.), *Solid blue 2 R and B* (G.) (O.), *Blue CB* (D. & H.), *Nigrosin, soluble in water* (Ber.) (G.) (F.) (K.) (D. & H.) (D.), *Sloleine*, *Bengale blue* (K.), *Grey*. Produced by the action of concentrated sulphuric acid on the insoluble indulines. The *indulines* are usually bronzy powders, the *nigrosines* black lustrous powders. Both are soluble in water, with a blue or red-violet colour. In concentrated H_2SO_4, they give a violet or blue solution, which becomes redder on dilution.

Application.—Acid colours. Dye *wool* in shades varying from greyish- or blackish-violet to indigo-blue, from a slightly acid bath. Special precautions have to be taken in order that level colours may be obtained.

Fast blue 6 B (Ber.) produces a much brighter blue than other indulines.

INDULINE SCARLET (B.). An azine dye. *Ethyl beta-methyl rosinduline hydrochloride.* 1892. Red powder, soluble in water. In concentrated H_2SO_4, red solution ; on dilution,

Application.—A basic colour. Dyes tannin-mordanted *cotton* scarlet red. Chiefly used in *calico* printing.

INGRAIN COLOURS. This term is applied to colours which are actually formed *upon the fibre* by chemical reactions. The process, with few exceptions, is applicable only to vegetable fibres. The term includes

the azo colours of the *paranitraniline red* type and the *primuline* dyes. The mineral dyes—*iron buff, Prussian blue, chrome orange, &c.*—are also true "ingrain colours," but the mordant dyes, although produced in a somewhat analogous manner, should be excluded. *v.* also Azo Colours on Cotton and Primuline.

INTENSIVE BLUE (By.), An acid blue of great colouring power.

IODEOSIN B *v.* Erythrosine.

IODEOSIN G *v.* Erythrosine G.

IODINE GREEN. *Night green, Pomona green, Light green.* A rosaniline derivative. *Zinc chloride double salt of hepta-methylrosaniline chloride.* 1866. Dark green powder, easily soluble in water. In concentrated H_2SO_4, reddish-yellow solution, which becomes pale yellowish-green on dilution.

Application.—A basic dye. Used to a small extent in *silk* dyeing.

IODINE VIOLET. Old name for Hofmann's Violet.

IRIS BLUE (B.) *v.* Fluorescent Blue.

IRON, Fe = 56. Iron occurs in the metallic state in meteorites. The chief ores of iron are *magnetic oxide*, Fe_3O_4; *red* and *brown hæmatite*, Fe_2O_3; *spathic ore*, and *clay ironstone*, more or less impure $FeCO_3$. The metal is obtained by roasting the ores and reducing the oxide by means of carbon in the form of coal or coke, and limestone. Pure iron may be produced by reducing heated oxide of iron in a stream of hydrogen—

$$Fe_2O_3 + 3H_2 = 2Fe + 3H_2O.$$
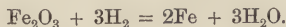
Iron has a specific gravity of 7·78, and melts at a temperature of about 1800° C. It turns rusty—*i.e.*, becomes oxidised—in moist air, the carbon dioxide present assisting in the reaction. Metallic iron is attracted by a magnet.

At a red heat, iron is decomposed by means of steam, hydrogen being evolved—

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2.$$

Iron is soluble in dilute acids, sulphuric and hydrochloric acids yielding hydrogen. Strong nitric acid liberates nitric oxide (NO). If the metal be treated with strong nitric acid, and then well washed, the treated surface becomes *passive*, and is only slowly attacked by acids. Dilute nitric acid dissolves iron with formation of ferrous nitrate and ammonium nitrate.

FERROUS SALTS.—The ferrous compounds when anhydrous are white, but on hydration they become green. On exposure to the air they become oxidised to the ferric state ($2FeO + O = Fe_2O_3$). They have, when in solution, an inky metallic taste. Ferrous salts are strong reducing agents, ferrous sulphate being used as such in the indigo vat. Nitric oxide is absorbed by solutions of ferrous salts, the resulting compound being brownish-black. This reaction is made use of as a test for nitric acid in qualitative analysis.

Solutions of ferrous salts have an acid reaction, and turn brown on exposure to the air, basic ferric salts being precipitated. Caustic soda or lime-water precipitates ferrous hydrate, and ammonium sulphide forms black ferrous sulphide (FeS) when added to aqueous solutions of ferrous salts.

When treated with potassium ferrocyanide a white precipitate, rapidly becoming blue, is formed, while ferricyanide of potassium at once yields a blue precipitate (Turnbull's blue).

Ferrous Acetate, $Fe(C_2H_3O_2)_2 + 4H_2O$.—Ferrous acetate may be obtained by the double decomposition of lead or calcium acetate and ferrous sulphate solutions. Acetic acid dissolves iron with formation of the same substance. The salt crystallises in green monoclinic prisms, which quickly oxidise on exposure to air to basic ferric acetate, hence its solution is too unstable to be used as a mordant.

Pyrolignite of Iron, *Iron liquor* or *Black liquor.*—This substance is an impure ferrous acetate, which in practice is found much more stable than the pure substance, and is a very useful mordant.

Preparation.—Pyrolignite of iron is prepared by treating pyroligneous acid (crude acetic acid) with scrap iron. The tarry matters which rise to the surface of the black liquid are removed. The liquid has a peculiar smell and a metallic taste.

It has a strength of 20 – 30° Tw., and contains, besides its essential ingredient, a small amount of ferric acetate and more or less tarry matter.

Moyret considers that the iron salt of pyrocatechin, which is present, together with other empyreumatic substances, prevents the oxidation of the liquid.

The specific gravity of the solution is often raised by the addition of ferrous sulphate or tannin.

Pyrolignite of iron is used in *cotton* dyeing, in greater quantities in *calico* printing, and in black *silk* dyeing.

Analysis.—The best practical method of ascertaining the value of acetate of iron is to make careful dye-trials, as with ferric sulphate.

The total amount of iron is estimated by evaporating about 5 grms. to dryness in a platinum dish, and gently igniting the residue to destroy organic matter. When cold, the residue is dissolved in hydrochloric acid, and the iron precipitated with ammonia or reduced by means of zinc, and titrated with potassium permanganate.

The total acetic acid may be determined as in aluminium acetate (*q.v.*).

Impurities.—Commercial acetate of iron may contain an excess of acetic acid, ferrous sulphate (often in quantity), ferric sulphate, ferrous chloride, sodium sulphate, sodium chloride, calcium and lead acetates. The amount of ferrous sulphate or ferrous chloride, in the absence of alkaline salts, may be determined by estimating the sulphuric or hydrochloric acid present.

Ferrous Bisulphite may be prepared by mixing concentrated solutions of sodium bisulphite and ferrous sulphate. Its use as a *cotton* mordant has been recommended. The material is saturated with the solution and steamed.

Ferrous Carbonate, $FeCO_3$.—This compound occurs in *spathic iron ore* and *clay ironstone*. Water containing carbon dioxide has a solvent action on ferrous carbonate, consequently it is found in mineral waters containing iron. The aqueous solution is decomposed on standing in the air or on boiling, with formation of hydrated oxides. If ferrous salts in solution are treated with carbonate of soda, ferrous carbonate in the form of a voluminous white precipitate is thrown down.

Ferrous Chloride, $FeCl_2$, *Muriate of Iron,* is formed as a by-product in the extraction of copper from spent oxide in the wet process. It is generally prepared by dissolving iron in hydrochloric acid, and crystallises from the liquid as green crystals having the composition $FeCl_2 + 4H_2O$. This substance is deliquescent in moist air.

Ferrous chloride is used in *wool*-printing for the production of logwood black.

Ferrous Hydroxide, $Fe(OH)_2$, is precipitated by caustic alkalies from ferrous salts as a white substance which quickly changes to green in the air. It is slightly soluble in water, and has an alkaline reaction.

Ferrous Nitrate, $Fe(NO_3)_2$, is prepared by treating iron with cold dilute nitric acid (1·11 sp. gr.). The compound has not been isolated as the solution is decomposed on warming, basic ferric nitrate being formed. Ferrous nitrate is also formed by the action of barium nitrate on ferrous sulphate.

Ferrous Oxalate, $FeC_2O_4 + 2H_2O$, is formed by treating a strong solution of oxalic acid with ferrous sulphate. It is a yellow crystalline powder, almost insoluble in water.

Ferrous Oxide, FeO, is a black powder, which is further oxidised on warming in air.

Ferrous Sulphate, $FeSO_4 + 7H_2O$, *Green vitriol, Copperas.*

Preparation—Ferrous sulphate is obtained as a by-product in the preparation of alum from shale containing iron pyrites, and also in the manufacture of copper sulphate. It is made on the large scale by dissolving scrap iron in dilute sulphuric acid, concentrating the solution and crystallising. Green vitriol is prepared also by the oxidation of iron pyrites, FeS_2, by exposure to the air and the action of moisture. The liquors which collect are boiled with scrap iron to reduce the ferric sulphate to ferrous sulphate, and then evaporated and crystallised.

Properties.—Ferrous sulphate forms green crystals which effloresce slightly in the air and become coated with a brown layer of basic ferric sulphate.

The salt is insoluble in absolute alcohol. 100 parts of water dissolve 70 parts of the crystals at 15° C., and 333 parts at 100° C. At a temperature of 100° C. the salt loses 6 molecules of water, forming a white powder, and the last molecule at 300° C., at which temperature slight decomposition takes place. On further heating, the residue decomposes thus—

$$2FeSO_4 = Fe_2O_3 + SO_3 + SO_2.$$

Ferrous sulphate solutions do not dissociate either on heating or on diluting, but long continued boiling causes oxidation and precipitation of basic ferric sulphates.

Large crystals are liable to contain free acid by enclosing some of the mother-liquor.

Ferrous sulphate should be free from copper and alumina.

Uses.—Green vitriol is extensively used in many industries. It is one of the oldest mordants known, and is largely used in *wool* dyeing. It is employed to a considerable extent also in cotton dyeing, for the production of Prussian blue in *calico* printing, and for the formation of *chamois*, a yellowish-brown colour on *cotton* by the action of soda. It also finds application in the manufacture of inks and pigments.

For some purposes the partially oxidised crystals which have become yellowish are preferred, but for *vat indigo dyeing* the ferric sulphate is a useless material.

Analysis. — *Ferrous iron* is readily estimated, either by a standard solution of bichromate or of permanganate of potash. The estimation by bichromate is merely the reverse of the method described for *Chromic Acid* (p. 87). The estimation by permanganate is carried out as follows :—

Preparation of Decinormal Permanganate Solution.—3·156 grms. of pure dry potassium permanganate are dissolved in a litre of distilled water. The solution requires standardising, since perfectly pure potassium permanganate is not easily obtainable. This is most readily performed by means of *pure* granulated ferrous ammónium sulphate (*q.v.*). 0·7 grm. of this salt (= 0·1 grm. of iron) is dissolved in about 100 c.c. of water in a porcelain basin, and 50 c.c. of a 10 per cent. solution of sulphuric acid added. The permanganate solution is now gradually run in from a burette, with constant stirring, until

the liquid acquires a faint pink colour. If strictly decinormal, 17·85 c.c. will be required. Instead of taking ferrous ammonium sulphate, the permanganate may be standardised by means of pure clean iron wire. 0·1 grm. is introduced into a small flask fitted with a bent glass tube and Bunsen's valve (see below, *Estimation of Total Iron*), and dissolved in dilute sulphuric acid. When dissolved, the liquid is allowed to cool, and titrated with the permanganate solution, as above described, and an allowance made (usually about ·4 per cent.) for impurities in the wire.

Estimation of Ferrous Oxide.—1 grm. of the sample of ferrous sulphate is dissolved in about 100 c.c. of water, or 100 c.c. of a 1 per cent. solution taken, and 50 c.c. of a 10 per cent. solution of sulphuric acid added. The solution is then titrated in a porcelain dish with $\frac{N}{10}$ potassium permanganate until a faint pink colour remains after stirring for about half a minute.

1 c.c. of $\frac{N}{10}$ permanganate = 0·0072 grm. of FeO, or 0·0278 grm. of $FeSO_4$, $7H_2O$.

Estimation of Total Iron.—1 grm. is washed into a small flask with about 50 c.c. of water; 10 c.c. of strong sulphuric acid and some zinc free from iron are then introduced. The flask is fitted with a cork and bent glass tube, to which is attached a Bunsen's valve. The latter consists of a short piece of india-rubber tubing closed at one end with a glass rod and having a longitudinal slit in the centre. Steam and hydrogen can by this arrangement easily escape from the flask, but air is unable to enter. The flask is inclined at an angle of about 45° and gently heated. When the reduction is complete (known by a drop of the liquid producing no coloration with a drop of potassium thiocyanate), recently boiled cold water is allowed to enter the flask, and the liquid titrated with $\frac{N}{10}$ permanganate as above. If the zinc has not thoroughly dissolved, it must be carefully removed and washed before titrating with permanganate. The difference between this titration and the direct titration represents the amount of iron present in the ferric state.

1 c.c. of $\frac{N}{10}$ permanganate = 0·008 grm. of Fe_2O_3.

Alumina may be detected in ferrous sulphate by boiling with the addition of sulphuric and nitric acids to oxidise the iron, and adding an excess of *pure* caustic soda. The liquor is boiled and filtered, and to the filtrate hydrochloric acid and ammonia added, when, if alumina be present, a white gelatinous precipitate will be obtained. The latter may be filtered off, washed, dried, ignited, and weighed as Al_2O_3.

Ferrous ammonium sulphate has a composition represented by the formula

$$FeSO_4 . (NH_4)_2SO_4 + 6H_2O,$$
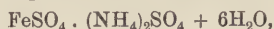
and contains exactly one-seventh of its weight in iron. It is prepared by mixing equivalent proportions of pure ferrous sulphate and ammonium sulphate (dissolved separately) and allowing the double salt to crystallise out. It occurs in commerce in crystals and in a fine granulated form. It should be tested for *ferric* iron by dissolving a little in water and adding potassium thiocyanate; no red colour should result. It should be preserved in a well-stoppered bottle.

The *pure* substance (which is permanent in air), as required for testing standard permanganate solutions, is prepared as follows:—A quantity of the commercial salt (free from ferric iron) is finely powdered, and a cold saturated solution made. After filtering into a large basin, *purified* alcohol is added with continual stirring until no further precipitate results. The mother liquor is decanted and the precipitate thoroughly washed with alcohol on a linen filter on a perforated plate, using the filter pump. After draining completely, the salt is removed to a flat dish and exposed to the air (carefully protected from dust), being turned over occasionally and eventually pulverised. As soon as the smell of alcohol has completely disappeared, the salt is transferred to a stoppered bottle. A weighed amount of this salt dissolved in water, with the addition of a little sulphuric acid, and oxidised with nitric acid should give on precipitation with ammonia the theoretical quantity of iron.

Ferrous Thiosulphate or Hyposulphite, FeS_2O_3, is formed on adding ferrous sulphate solution to sodium thiosulphate, $Na_2S_2O_3$. It has been suggested as a cotton mordant, but has not been largely used. The salt oxidises slowly on the fibre, forming ferrous and eventually ferric sulphate.

FERRIC SALTS.—Solutions of ferric salts are generally yellow or reddish-brown in colour, and have an astringent, metallic taste. Ferric salts result from the action of oxidising agents like chlorine or nitric acid on ferrous salts. Zinc, iron, or sulphuretted hydrogen reduce the ferric salts to the ferrous condition.

Lime and the caustic and carbonated alkalies produce with ferric salts a reddish-brown precipitate of ferric hydrate, insoluble in excess of the alkali or in ammonia. The presence of tartaric acid, sugar, &c., prevents its precipitation. Ammonium sulphide and hydrogen sulphide (if the iron salt be alkaline) cause the formation of black ferrous sulphide, FeS (mixed with sulphur), which is soluble in dilute acids leaving a residue of

sulphur. Ferric salts give a blue precipitate with potassium ferrocyanide, which is insoluble in hydrochloric acid, but is decomposed by caustic alkalies. Potassium ferricyanide causes a reddish-brown coloration but *no precipitate;* the formation of a blue precipitate in such solutions indicates the presence of ferrous salts.

Acid solutions of ferric salts produce with potassium sulphocyanide a blood-red coloration, which does not disappear on heating with a little alcohol (test for presence of ferric salts in ferrous salts). An excess of acid should be used if acetates, oxalates, or fluorides are present. The ferric sulphocyanate, $Fe_2(CNS)_6$, may be extracted by shaking with ether to which it imparts its red colour. Very dilute solutions of ferric salts show the coloration when treated with freshly-prepared potassium sulphocyanide solution.

Ferric Acetate, $Fe_2(C_2H_3O_2)_6$, is prepared by treating a solution of ferric sulphate with lead acetate. Dark red crystals of the salt, containing 2 molecules of water separate from the solution. On the addition of an alkaline carbonate to the solution of the normal salt, basic acetates are formed. The normal salt does not dissociate on heating or diluting, but the basic salts are dissociated and the iron precipitated on boiling. The more basic salts are the most unstable, though mere dilution with water does not affect them. Ferric acetates have been replaced by nitrate of iron in silk dyeing, for which they were formerly much used.

Ferric Nitrate Acetate. — This substance is used in the form of a solution as a mordant for the black-dyeing of *silk* intended for plush, as the colour thus obtained is not affected by hot pressing. It is prepared by adding iron turnings in excess to nitric acid. The pasty mass of basic ferric nitrate is treated with a quantity of hot acetic acid insufficient to dissolve it. The dark-red liquid is allowed to cool and settle, and the clear solution is ready for use.

Ferric Arsenate. — On the addition of sodium arsenate to solutions of ferric salts, a white precipitate of ferric arsenate, $Fe_2(AsO_4)_2$, is produced. It is insoluble in acetic acid. The reaction is employed for fixing iron mordants on cotton in alizarin dyeing.

Ferric Chloride, Fe_2Cl_6. — The anhydrous salt is obtained by passing chlorine over red-hot iron. It forms yellow scales which have a metallic lustre. The crystals can be sublimed and are soluble in water, alcohol, and ether. It is very deliquescent. It is prepared in solution by dissolving iron in hydrochloric acid and oxidising the ferrous chloride formed by means of chlorine. The aqueous solution dissociates on heating, but if not too

dilute the normal salt is re-produced on cooling. The concentrated solution is dark brown and viscid. Basic chlorides in the form of dark red solutions, which are very stable, are produced by dissolving freshly precipitated ferric hydrate in ferric chloride.

Both the normal and basic ferric chlorides dissociate too slowly to be applicable in dyeing.

Ferric Hydroxide or **Ferric Hydrate,** $Fe_2(OH)_6$. — Caustic alkalies precipitate ferric hydrate as a red-brown flocculent mass from solutions of ferric salts. Boiling causes the hydroxide to lose 1 molecule of water, forming $Fe_2O(OH)_4$. The presence of glycerin and other organic substances impedes the precipitation of the hydrate. An alkaline solution of ferric hydrate and glycerin has been suggested as a mordant for *cotton.* Ferric hydroxide is soluble in dilute acids, in ferric chloride, and ferric acetate; ammonia and caustic alkalies have no effect on it.

Ferric hydrate has no affinity for textile fibres.

Alkaline Iron Mordants. — Although ferric hydrate is insoluble in caustic alkalies, solutions of it may be prepared in the form of dark red liquids by adding glycerin or glucose to solutions of ferric salts, and then adding the caustic alkali. An alkaline solution of ferric hydrate which readily dissociates is thus formed.

Ferrous sulphate has also been used in place of a ferric salt.

The alkaline mordants have not been much used owing to their excessive alkalinity.

Koechlin* (*l.c.*) recommends 2 parts of nitrate of iron (76 Tw.), 2 parts of caustic soda (66° Tw.), and 1 part of glycerin (48° Tw.).

Ferric Nitrate, $Fe_2(NO_3)_6$. — Ferric nitrate is commercially known as "pure nitrate of iron," the term "nitrate of iron" being applied to a solution of ferric sulphate. Ferric nitrate is prepared by dissolving scrap iron in nitric acid until basic ferric nitrate commences to separate. The composition of the resulting liquor varies. It is used to some extent in silk dyeing and for the production of iron-buff shades on cotton.

Ferric Oxalate, $Fe_2(C_2O_4)_3$. — This salt dissolves in water, forming a green solution which is partly reduced to ferrous oxalate by boiling.

Ferric Oxide, Fe_2O_3. — *Iron Sesquioxide.* — Ferric oxide occurs as *hæmatite* and as *specular iron ore,* &c. It is also obtained as *rouge* by the calcination of ferrous sulphate. It dissolves slowly in acids. On heating ferric hydrate this oxide is formed as a red-brown powder.

Ferric Phosphates. — Ferric phosphate, $FePO_4$, is formed as a white precipitate on

* *Journ. Soc. Dyers and Col.*, 1885, pp. 147 and 188.

the addition of sodium phosphate to ferric salts. Acetic acid does not dissolve it, but it is soluble in mineral acids. The addition of sodium acetate causes the complete precipitation of the phosphate. Iron mordants are fixed by means of sodium phosphate in accordance with this reaction.

Persoz has recommended ferric pyrophosphate, $Fe_4(P_2O_7)_3$, in ammoniacal solution as a cotton mordant.

Ferric Sulphate, $Fe_2(SO_4)_3$.

Preparation.—The normal sulphate is prepared by treating a warm solution of ferrous sulphate, dissolved in sulphuric acid of the necessary dilution, with nitric acid. The amounts used should correspond with the equation—

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 = 3Fe_2(SO_4)_3 + 2NO + 4H_2O.$$
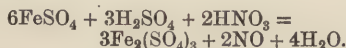
The mixture is heated, if necessary, and then allowed to cool and settle. The resulting solution has a yellowish-brown colour, and if sufficiently concentrated, crystals of the normal salt separate from the liquid. The concentrated solution is dehydrated by sulphuric acid, anhydrous ferric sulphate being thrown down. By the addition of alkalies or on boiling the diluted solution of ferric sulphate, or on oxidation by exposure to the air, basic ferric sulphates are formed.

Ferric sulphate is the principal constituent of the so-called "*nitrate of iron.*"

The normal salt is employed to some extent in *cotton* dyeing.

"*Nitrate of Iron*" (Fr. rouille).

Preparation.—This substance which contains no ferric or ferrous nitrate, and is hence incorrectly termed "nitrate of iron," is prepared in a similar manner to normal ferric sulphate, the amount of sulphuric acid required for the above equation being reduced by half. The resulting product contains normal and basic ferric sulphates; and normal and basic ferric sulphate nitrates — viz., $Fe_2(SO_4)_2NO_3)_2$ and $Fe_2(SO_4)_2(NO_3)(OH)$ are formed if the amount of nitric acid is increased. Basic ferric sulphates prepared by adding caustic soda to a solution of normal ferric sulphate dissociate after standing a few hours. More stable but more expensive products are obtained by dissolving ferric hydrate in normal ferric sulphate solution.

The commercial products vary in composition, but Moyret finds that those corresponding to the formula $Fe_4(SO_4)_5(OH)_2$ give good results in silk dyeing. A compound corresponding to this formula is prepared according to the equation—

$$12FeSO_4 + 3H_2SO_4 + 4HNO_3 = 3Fe_4(SO_4)_5(OH)_2 + 4NO + 2H_2O.$$
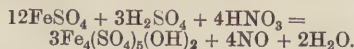
Moyret gives the following method for the preparation of this particular product :—

A stone cistern provided with a chimney and a mixer are required. In this tank are placed 72 parts of ferrous sulphate and a mixture of $6\frac{1}{2}$ parts of sulphuric acid (168° Tw.), and $12\frac{1}{2}$ parts of nitric acid (67° Tw.) diluted with a little water. The mixture should be added gradually and the mass stirred. When no further reaction takes place the mass is heated for a short time by means of steam. A mordant having a composition intermediate between $Fe_2(SO_4)_3$ and $Fe_4(SO_4)_5(OH)_2$ also gives good results.

Properties.—"Nitrate of iron" has a dark red colour, and should contain 12 to 16 per cent. of ferric oxide when dried and ignited. Ferrous sulphate and chloride or sulphate of sodium are objectionable. Free nitric acid in more or less quantity is usually present. Dilution of the solution causes precipitation of a still more basic salt. Commercial products having the same composition often vary in their properties, especially for silk dyeing; and their value is best estimated by comparative dye trials. If intended for cotton dyeing the following plan may be adopted :—swatches of calico or cotton yarn, each weighing 10 grms., are thoroughly wetted out and worked together for about an hour in a decoction of sumach or myrabolams. The swatches are taken out, the excess of liquid removed by shaking, and each piece put into a dilute solution (5 c.c. in 250 c.c.) of the sample of "nitrate of iron" to be examined. After thirty minutes the pieces are taken out, well washed, dried, and compared.

ANALYSIS.—Solutions of "nitrate of iron" usually have a strength of about 80° Tw., and contain about 9 to 11 per cent. of iron.

Estimation of Total Iron.—25 c.c. (measured in a specific gravity bottle and weighed) are diluted to 500 c.c. 25 c.c. are withdrawn and diluted to about 200 c.c. If any iron is present in the ferrous state (in which case potassium ferricyanide will give a blue precipitate with the sample), it is preferable to add a few drops of nitric acid, and boil for some minutes. A slight excess of ammonia is added, and the liquid filtered. The precipitate should be washed several times with hot water by decantation before bringing it wholly on the filter. The precipitate may be either dried, ignited, and weighed as Fe_2O_3, or dissolved while still moist in sulphuric acid, reduced by zinc, and titrated with $\frac{N}{10}$ permanganate, as given under ferrous sulphate.

In the absence of nitric acid or nitrates, the 25 c.c. of the diluted solution may be reduced direct, and titrated with potassium permanganate.

1 c.c. of $\frac{N}{10}$ permanganate = 0·0056 grm. of Fe.

Estimation of Ferrous Iron.—5 to 10 c.c. of the sample are weighed, diluted with water, and acidulated with sulphuric acid. The solution is then titrated with $\frac{N}{10}$ permanganate.

$$1 \text{ c.c.} = 0.0056 \text{ grm. of Fe, or}$$
$$0.0072 \text{ grm. of FeO.}$$

The amount of ferric oxide is obtained by deducting ferrous iron from the total, and calculating into Fe_2O_3.

Sulphuric acid is best determined by acidulating the filtrate from the ferric oxide precipitate with hydrochloric acid and adding barium chloride. If barium chloride is added direct to the ferric sulphate solution, the barium sulphate is liable to be contaminated with iron.

Hydrochloric acid should also be determined, after removal of the oxide of iron by ammonia, by acidulating the solution with nitric acid and adding silver nitrate.

Sodium salts may be detected and estimated by adding ammonia, filtering, evaporating the filtrate to dryness, and igniting the residue. If iron compounds only were present, nothing more than a trace would remain after ignition. Sodium nitrate is used as an adulterant.

Aluminium, if present, may be detected by the tests mentioned under *Analysis of ferrous sulphate*.

Relation of Acid to Base.—In the analysis of ferric sulphate one of the most important matters is to determine the relative proportion of total acid and ferric oxide present. For most purposes, commercial "nitrate of iron" or ferric sulphate should contain less acid than that necessary to form normal ferric sulphate. Some samples contain an excess of acid. The amount of acid in combination with iron (as well as any free acid, if present) is best determined by taking 2 to 5 grms. of the sample, diluting with about 200 c.c. of water, and adding a slight excess of normal solution of sodium carbonate. The liquid is boiled and filtered, and the precipitate well washed with hot water. The excess of sodium carbonate is then estimated by normal sulphuric acid and methyl-orange. Each c.c. of normal sodium carbonate = 0.040 grm. of SO_3.

Example.—2.5 c.c. = 3.50 grms. of ferric sulphate were treated with 22 c.c. of normal Na_2CO_3. The filtrate required 4 c.c. of normal H_2SO_4.

$$\therefore \quad \frac{0.040 \times 18 \times 100}{3.56} = 20.22 \text{ per cent. of } SO_3,$$

combined with ferric and ferrous oxides.

The amount of SO_3 required to combine with the found percentages of ferric and ferrous oxides to form normal sulphates is calculated and compared with the actual amount of acid present. Instead of using sodium carbonate, boiling and filtering as above given, fairly good results may be obtained by titrating direct with normal caustic soda and phenolphthaleïn, as in the *Analysis of tin mordants* (*q.v.*); but the end reaction is not very distinct.

The following figures show the results of analyses of a few samples of average ferric sulphate or "nitrate of iron":—

	1	2	3	4
Specific Gravity, . . .	1.410	1.402	1.405	1.345
Equal to Degs. Twaddell,	82°	80°	81°	69°
Total iron, ...	11.80	10.88	10.97	9.59
Ferric oxide, ...	16.86	15.45	12.00	12.72
Ferrous oxide, . . .	..	0.15	3.32	0.86
Sulphuric acid (SO_3), . .	16.61	17.20	16.75	16.20
Hydrochloric acid (HCl), .	1.64	0.06	..	..
Total acid combined with iron in terms of SO_3, .	20.05	17.30	16.96	16.40
Calculated SO_3 required to form normal sulphates,	25.30	23.39	22.74	20.31

Ferric sulphate-nitrates are also sold under the name of nitrate of iron. They are prepared according to the method indicated above. In oxidising ferrous sulphate, the sulphuric acid is partly, or entirely, replaced by nitric acid. The products are deep brownish-red solutions of varying composition, and frequently contain ferrous salt. In cotton dyeing, an admixture of the latter salt is sometimes advantageous. The value is also determined by the results they give in experimental dyeing. The ferric sulphate-nitrates are used almost exclusively in cotton dyeing. On the whole, "nitrate of iron" brands, which are used for cotton, are slightly less basic than those made for silk dyeing.

Iron Alum or **Potassium Ferric Sulphate**, $Fe_2(SO_4)_3K_2SO_4 + 24H_2O$, forms light-violet octahedra, and is soluble in about 5 parts of cold water. It is analogous to ordinary alum. Iron alum is not used to any great extent in dyeing.

Ferric Sulphocyanide or **Thiocyanate**, $Fe_2(CNS)_6$, is produced as a blood-red coloration by treating ferric salts with sulphocyanides.

IRON-BUFF and NANKIN-YELLOW.— These two colours, which differ only in the depth of shade, consist of hydrated ferric oxide, and they resemble certain kinds of ochre. Iron-buff and Nankin-yellow are produced by precipitating a ferrous or ferric salt with an alkali or alkaline carbonate; in the case of a ferrous salt being used, the resulting ferrous hydroxide is oxidised subsequently by the air or by such oxidising agents as chloride of lime to ferric hydroxide.

The iron-buffs are chiefly dyed on cotton, yielding from yellow to light brown shades which are fast to light, soap, and alkalies, but are sensitive to the action of acids. The shades are produced by the methods employed for the fixation of iron mordants on cotton. Pure shades cannot be obtained with pyrolignite of iron on account of the tarry matter it contains ; pure acetate of iron can be used. The shades should be fixed with the ordinary mineral fixing salts, such as silicate, phosphate or arsenate of soda. For the oxidation of the ferrous salts or hydroxide a passage through a solution of chloride of lime is of advantage. Concentrated ferrous solutions have a weakening effect on the cotton fibre, especially if the oxidation proceeds rapidly, and this fact must not be lost sight of. If a highly diluted solution of a ferric salt is used, some glycerin should be added to prevent a dissociation of the salt. The dyeing process can be repeated for the production of fuller shades.

ISORUBIN (Ber.). *v.* New Magenta (M.).

ITALIAN GREEN (Lepetit and Dolfus). A colour allied to Cachou de Laval, and obtained by the action of *sulphur, caustic soda, and copper sulphate on paranitrophenol.* 1895. Black mass, slightly soluble in water with a green colour. In concentrated H_2SO_4, the dye is decomposed with precipitation of sulphur and evolution of sulphuretted hydrogen.

Application.—Dyes *cotton* dark green from a salt bath.

J

JACKWOOD (*Artocarpus integrifolia*) is a well-known tree cultivated in India, Burmah, and Ceylon. It is exported to Europe as a furniture wood, but is used in India as a source of yellow dye for colouring the robes of the Burmese priests. It is applied with alum mordant, and has been shown to contain the same colouring matter as old fustic.[*]

JAMAICA WOOD *v.* Logwood.

JANUS COLOURS (M.). This series of dyes, introduced in 1897, form a new group of azo colours which possess at one and the same time strongly acid and strongly basic properties. In this respect they are almost unique amongst dyestuffs. Sulphonated basic dyes—*e.g.*, *Acid magenta*—contain both *acidic* (SO_3H) and *basic* (NH_2) groups, but the acid group so far overpowers the amido groups that the latter exert no influence upon the dyeing properties of the colours. Sulphonated azo compounds are, of course, extremely numerous, constituting the greatest number of the acid reds, oranges, yellows, &c. The number of azo dyes containing basic groups is, however, very limited

[*] A. G. Perkin, *Trans. Chem. Soc.*, 1895, p. 937.

(*Chrysoidine, Bismarck brown, Tannin orange, Atlas red*), and the Janus dyes are the first sulphonated basic azo dyes introduced.

JANUS BLUE G. Brownish-black powder. Aqueous solution, reddish-blue ; alcoholic solution, bright blue. Concentrated H_2SO_4, dirty yellow solution ; on dilution, olive-green, then reddish-blue.

JANUS BROWN B. Greenish-black powder, slightly soluble in water with light brown colour. Alcoholic solution, brownish-red. Concentrated H_2SO_4, dark green solution ; on dilution, reddish-blue, then brown.

JANUS GREEN B. Greenish-brown powder. Aqueous and alcoholic solution, bright blue. Concentrated H_2SO_4, olive-green solution ; on dilution, greenish-blue, then bright blue.

JANUS RED B. Reddish-brown powder. Aqueous solution, brownish-red ; alcoholic solution, bright red. Concentrated H_2SO_4, bluish-green ; on dilution, bluish-red to brownish-red.

JANUS YELLOW R. Orange-red powder. Aqueous solution, yellow ; alcoholic solution, slightly redder. Concentrated H_2SO_4, bluish-red ; on dilution, becomes red, then yellow.

JANUS BLACK 0, 1, 2.
JANUS BLUE R.
JANUS BROWN R.
JANUS CLARET RED B. 〉 Are other members of the group.
JANUS GREEN G.
JANUS GREY B.
JANUS ORANGE.

Application.—Acid and basic dyes, which possess the peculiar property of dyeing unmordanted *vegetable fibres* from a strongly acid solution.

Wool.—They are applied as ordinary acid colours, but are not specially valuable in wool dyeing. *Silk.*—Dye in a cold or slightly warm solution with addition of acetic acid. *Cotton.*—*1st method,* Dye as direct dyes, but with addition of sulphuric acid ; *2nd method,* dye as basic colours on tannin mordant ; *3rd method,* dye as in method 1, then fix in a bath containing tannic acid, tartar emetic, and oxalic acid ; *4th method,* dye as method 3, but dye and fix at the same time.

Process 3 gives the best results.

JAPANESE GALL NUTS *v.* Gall Nuts.
JAPONIC ACID *v.* Catechu.
JASMIN (G.) *v.* Curcumeïn (Ber.).
JET BLACK R (By.). An azo dye.

Alpha-naphthylamine 〈 *Amidobenzol disulphonic acid.* / *Phenyl alpha-naphthylamine.*

1888. Black powder, soluble in water with a violet colour. In concentrated H_2SO_4, blue solution ; on dilution, greenish-blue ppt.

Application.—An acid colour. Dyes *wool*

from a slightly acid or neutral bath, blue-black.

JUTE. This valuable fibre is the product of several species of *Corchorus*, and is indigenous to India. The most important species is *Corchorus capsularis*, which is grown to an enormous extent in India and Southern Asia generally. In India about 2,000,000 acres are under jute cultivation, and the value of the trade is said to be £10,000,000 sterling.*

The jute plant is an annual, growing 2 to 5 feet high. It is sown in March and gathered in June, and the separation of the fibre from the plant is extremely simple, no machinery of any kind being required. When the plants are ripe they are cut down and stripped of their leaves, twigs, and berries. The stems are then left to steep for a few days in running water, which simple process suffices to cause the bark to separate from the stem. The loose bark is then removed and the fibre separated by hand, well washed and hung up to dry. The fibre thus obtained is imported in bundles and is comparatively clean and pure.

Physical Properties.—There are numerous commercial varieties which differ in colour, fineness, and lustre, the best qualities having a pale golden colour and high lustre. The length of the raw fibre is 1½ to 2½ yards. About 12 to 18 inches of the bottom end is cut off and forms *jute butts* or *jute cuttings*, which is much esteemed as a raw material for the manufacture of paper. The fibre is then crushed in a press and softened with an oil emulsion, after which it is hackled and spun. The manufacture of jute is centered in Dundee, but latterly a number of factories have been started in India.

Jute is a very cheap fibre, but cannot be readily bleached. It rots somewhat easily when exposed to moisture, but is largely used in the manufacture of carpets, rugs, sacking, rope, &c. The commercial fibre consists of fibre bundles, the ultimate jute fibres being readily separated by treatment with caustic soda or chromic acid. They consist of cells which vary in length from 1·5 to 5 mm., and in diameter from 20 to 25 m.m.m. In transverse section they are usually five- or six-sided, the central lumen varying greatly in size.

Chemical Composition and Reactions—Jute differs essentially from the other important vegetable fibres in chemical composition and properties. It contains no free cellulose, but consists of a compound cellulose, *lignocellulose*. Jute lignocellulose is composed of oxidised cellulose in combination with *bastose*, the latter substance being itself resolvable into a furfurol yielding complex, and ketonic bodies. Cross and Bevan have proposed the name *corchorobastose* for the jute substance.

* D. Morris, Asst. Director of Kew.

Jute is coloured an intense brown by sulphuric acid and iodine, and a golden yellow by aniline sulphate. If treated with chlorine and then with sodium sulphite it develops a beautiful but evanescent crimson colour—a reaction also shown by tannin-mordanted cotton.

Jute readily absorbs chlorine or bromine and becomes chemically changed, the reaction consisting in the replacement of hydrogen by the halogen. The ordinary methods of bleaching adopted for other vegetable fibres are, therefore, not applicable to jute. It is frequently partially bleached by treatment with sulphurous acid.

In dyeing, jute behaves in a similar manner to tannin-mordanted cotton. It may thus be dyed direct with the basic colours, and this class of dye is mainly employed.

Counts.—The counts for jute yarn are the same as for linen.

K

KAMBE WOOD *v.* CAMWOOD.

"KAMELA" (Kamala)* is obtained from the fruit of the *Rottlera tinctoria*. It forms a reddish powder, often greatly adulterated, which is largely used in India as a medicine, and for dyeing silk a bright orange.

KAISER YELLOW. Old name for AURANTIA.

KAISER RED. Old name for EOSINE B N.

KATIGEN BLACK-BROWN (By.). A sulphide colour, giving dark browns on cotton. *v.* SULPHIDE COLOURS.

KAUTHOSINE J. and R. *v.* TOLUYLENE ORANGE G and R.

KERATIN *v.* WOOL.

KERMES. This dyestuff is of great antiquity, having been used by the Hebrews, and being mentioned by Moses. It seems probable that the Hebrew word several times translated "scarlet" in the Old Testament (Exodus xxvi., xxviii., xxxiv.) was used to designate the blood-red colour produced by kermes with alum mordant. This was one of the three colours prescribed to be used for the curtains of the Tabernacle and for colouring the "holy garments" of Aaron.

The term *granum*, which was given to kermes by Pliny, probably on account of its resemblance to a grain or berry, was adopted by more recent writers, and is the origin of the term, "ingrain colour," which is even now in use. The words "vermilion" and "crimson" are also derived respectively from the old Italian words *vermilicus* and *cremesimo*, the former of which signified the kermes

* See "The Constituents of the Indian Dyestuff Kamala," by A. G. Perkin, *Trans. Chem. Soc.*, 1893, p. 875.

14

insect, the latter being probably a corruption of the original Arabic *kermes* or *kremes*.

Kermes was in general use as a dyestuff in Europe as early as the tenth century. In Germany, from the ninth to the fourteenth century, the serfs were bound to deliver to the convents every year a certain quantity of kermes amongst other products of husbandry. It was collected from the oak trees on St. John's Day, between the hours of eleven and noon, with religious ceremony, and on this account it received the name of *Johannisblut* (St. John's blood). At that time a great deal of German kermes was sent to Venice to produce the "scarlet" to which that city gave its name.*

About the year 1550, cochineal was introduced into Europe, and since it is far richer in colouring matter than kermes it gradually superseded the older dyestuff, which has not been used to any extent in this country for at least 100 years. It is, however, still employed in some countries, to which it is indigenous—*e.g.*, Italy, Turkey, and Morocco.

Origin.—Kermes is derived from the insect *Coccus ilicis*, which is found principally upon the *Quercus coccifera*, or Ilex oak. The dyestuff consists of the dried insects, and is of similar appearance to cochineal, but the grains are larger. It contains only about one-tenth as much colouring matter, which is probably identical in chemical composition with that of cochineal.

One peculiarity of kermes is that it possesses a pleasant aromatic smell, which it also imparts to cloth dyed with it.

Application.—It is employed in exactly the same way as cochineal, and it has been frequently stated that it produces more permanent colours than that dyestuff, but there does not appear to be any foundation for this assertion.

KERMESIN ORANGE (L.) *v.* ORANGE I (K.).

KETONE BLUE 4 B N (M.). Reddish-blue liquid. Aqueous and alcoholic solution, bright blue. Concentrated H_2SO_4, brownish-yellow; on dilution, olive-green, then reddish-blue.

Application.—An acid colour. Dyes *wool* or *silk* bright blue.

KIESERITE *v.* MAGNESIUM SULPHATE.

KINO or GUM KINO is a resin somewhat allied to catechu (*q.v.*). It is produced by *Butea frondosa* and other plants. The flowers of *B. frondosa* are sold in India under the name "Tesso," and are employed for dyeing cotton yellow.

KNOPPERN or ACORN GALLS. These are produced by the sting of the *Cynips quercus calycis* upon *Quercus pedunculata* and other varieties of the oak. They are chiefly collected in Austria-Hungary, and contain 20

* Crace-Calvert, *Dyeing and Calico Printing.*

to 50 per cent. tannin. They are principally employed by tanners, not being much used in dyeing.

KRESOL RED (B.). *v.* CRESOL RED (B.).

KRYOGEN BLUE G, R (B.) and **KRYOGEN BROWN** (B.). 1899. Sulphide colours, giving respectively navy-blue and dark brown shades on cotton. *v.* SULPHIDE COLOURS.

L

LAC-DYE.—This substance, in the natural liquid form in which it exists in the lac cells, has been used by the natives of India and Persia from the earliest times. It was introduced into Europe about the end of the last century by the East India Company, and a good deal of the credit for its successful practical application is due to Bancroft.

Origin.—Like cochineal and kermes it is produced by a scale insect, being prepared along with shellac from incrustations formed by the *Coccus lacca* upon juniper and other similar trees. The incrustation is of a cellular character, each female insect forming and inhabiting a single cell, which is evidently intended for the protection of the eggs. The agglomeration of an immense number of these cells results in the smaller branches becoming thickly coated with the incrustation, and when removed from the trees, these twigs are known as "stick lac."

This product, therefore, consists of (1) woody matter (2), the resinous matter forming the cells, and (3) the colouring matter.

By passing between rollers the incrustation is readily separated from the twigs, and is then known as "seed lac;" but no definite information regarding the preparation of lac dye from this body is available. The resinous lac may be removed by heating the seed lac until it melts and then straining through a canvas cloth, and it is known as "shellac," "button lac," "garnet lac," &c., according to its mode of preparation and colour. It is one of the most valuable of the resins, and is largely employed in making varnishes, lacquers, stiffening for felt hats, &c.

Lac-dye is usually imported, chiefly from India, in the form of small flat cakes, about $2\frac{1}{2}$ inch square and $\frac{1}{2}$ inch thick, or as a powder. It is quite insoluble in water, being a calcium, aluminium, or tin lake of the colouring matter, and therefore before use must be treated with hydrochloric acid in order to remove the metallic base, and liberate the soluble colouring matter. In other respects, its application is similar to that of cochineal, but it does not produce such brilliant scarlet shades as that dyestuff. Its colouring power is from one-half to one-third of that of a good sample of cochineal.

LACMOID (INDICATOR) *v.* ACIDIMETRY.

LACTIC ACID, $C_3H_6O = CH_3.CH(OH)$
COOH. *Ethylidene* or *ordinary lactic acid.*
This acid is found during the fermentation of
various sugars (cane sugar, sugar of milk,
&c.) by the lactic ferment. Lactic acid is
present in sour milk.

Preparation.—Grape sugar, invert sugar,
or molasses may be used as a source of lactic
acid, but sour milk and also starch are more
often used. In the latter case, a boiled
solution of starch is mixed with 5 to 10 per
cent. of malt and kept at 65° C. for a few
days in wooden tanks. The contents of the
vessels (all of which require to be sterilised)
are boiled, saltpetre and phosphates added,
and when cooled to 35° C. some pure lactic
ferment is added. From time to time chalk
is added, and when the mixture no longer
turns acid, the contents are boiled, filtered,
and the solution of calcium lactate either
crystallised as such, or concentrated, treated
with dilute sulphuric acid, filtered from cal-
cium sulphate, and the filtered lactic acid
solution concentrated so that it may contain
50 to 70 per cent. of the acid.

Properties.—Lactic acid is a monobasic
acid. It has been obtained in the pure state,
with a melting point of 18° C. by distilling
the commercial acid at a pressure of 1 mm.

Commercial lactic acid is a syrup of specific
gravity 1·2, and containing at least 50 per
cent. lactic acid. It should be of a yellow-
brown colour (crude samples are brown or
black), and contain mere traces of albuminous
matter.

Lactic acid is weaker than tartaric or
oxalic acid, but is a more powerful reducing
agent than either. Both lactic acid and
almost all its salts (the lactates) are readily
soluble in water.

Lactic acid is used for dissolving dyestuffs,
such as the spirit soluble indulines. It is
sometimes employed for discharge effects
in calico-printing. In many cases, however,
its hygroscopic nature has an injurious effect
on the colours.

Lactic acid is now largely used as an assis-
tant in mordanting wool with bichromate
of potash. In some cases it can take the
place of glycerin both for printing and finish-
ing, and is very suitable for printing on
wool, except with acid dyestuffs.

Lactic acid has the advantage over oxalic
acid that it is non-poisonous, and over acetic
acid that it is non-volatile. It wets and pene-
trates both animal and vegetable fibres
similarly to glycerin.

C. Dreher* considers that lactic acid can
be advantageously used in the mordanting
of hard milled stuffs, greasy wools, &c.

A double lactate of antimony and calcium
is used for mordanting cotton.

Analysis.—F. Ulzer and H. Seidel* dis-
solve 1 grm. of the sample in 10 c.c. of water,
containing 3 grms. of caustic potash, and
add gradually, with continual shaking, a 5
per cent. solution of potassium permanganate
until the liquid has no longer a green but a
bluish-black colour (which must not dis-
appear on boiling); they then decolorise by
the addition of hydrogen peroxide or sul-
phurous acid, filter, acidify with dilute sul-
phuric acid, and titrate the oxalic acid thus
produced with standard permanganate solu-
tion. It is assumed that the lactic acid
has been oxidised in accordance with the
equation—

$$C_3H_6O_3 + 5O = C_2H_2O_4 + 2H_2O + CO_2.$$

In this way a sample of "chemically pure"
lactic acid was found to contain 90·13 per
cent. $C_3H_6O_3$; by boiling with excess of stan-
dard caustic potash and titrating the excess,
89·50 was found. The same sample gave only
74·05 per cent. when titrated with potassium
hydrate in the cold, so that it must have
contained a large amount of lactone anhy-
dride; a commercial sample was found to
contain an even larger amount.

"LACTOLINE" is a mixture of about
1 molecule of potassium lactate and 1 molecule
of free lactic acid. It generally contains
gummy material such as dextrin. It is used
as a substitute for tartar.

LAEVULINIC ACID, $C_5H_8O_3 = CH_3CO$
$CH_2CH_2COOH.$—Laevulinic acid is produced
by the action of acids on cane sugar, levulose,
cellulose, starch, and other carbohydrates.

Laevulinic acid crystallises in scales which
melt at 33° C. and boil at 239° C. It is very
soluble in water and in alcohol. It is a mono-
basic acid.

At the present time laevulinic acid is little
used in calico printing; its employment
as a solvent for induline has been patented
by the Hoechst Colour Works. It may pos-
sibly replace oxalic, tartaric, and citric acid
in some cases.

**LANACYL BLUE B B, R, LANACYL
NAVY BLUE, and LANACYL VIOLET B**
(C.). Acid dyes which produce navy blues
and dark reddish-blues which do not rub off.

LANAFUCHSINE S B, S G (C.). Easily
levelling bright acid reds.

LANCASTER YELLOW. An obsolete
acid dye. *Dinitrophenol azopheno'.*

LANUGINIC ACID *v.* WOOL.

LAUTH'S VIOLET. *Thionine.* An obso-
lete thiazine basic dye.

LEAD, Pb = 206·5. The principal ores of
lead are *galena*, PbS, and *cerussite*, $PbCO_3$.

Preparation.—In order to extract the metal,
the ore is picked, crushed, washed, and then
smelted in furnaces. The oxide, sulphate,
and sulphide of lead react on each other,

forming sulphur dioxide and metallic lead. The crude lead is afterwards freed from other metals by melting in contact with air ; the foreign metals being oxidised and forming a scum which is skimmed off.

Properties.—Lead is a bluish-white metal, showing a bright surface when freshly cut, but quickly tarnishing in moist air, owing to the formation of a film of lead oxide. The specific gravity of the metal is 11·37. It is very soft and very malleable. Lead melts at 330° C., and a layer of oxide rapidly forms on the surface of the fluid metal. In contact with pure water and air lead becomes oxidised to hydroxide, $Pb(OH)_2$, which is somewhat soluble in water. Natural waters which contain small quantities of carbon dioxide and mineral salts cause the lead to become covered with a coating of sulphate and carbonate of lead which preserve the metal from further attack. Excess of carbon dioxide causes partial solution of the carbonate.

At ordinary temperatures acetic acid and dilute nitric acid attack lead. Concentrated sulphuric acid has little action on sheet lead. Finely divided lead is attacked by hydrochloric acid, but the reaction on sheet lead is not so energetic.

Lead is a constituent of many alloys, such as solder, pewter, type metal, &c.

LEAD ACETATE, $Pb(C_2H_3O_2)_2 + 3H_2O$. *Sugar of lead.*

Preparation.—*White acetate of lead* is made from acetic acid by treating the liquid with litharge (PbO) in small quantities with constant agitation in a lead tank until nearly neutral. The liquid is then heated to boiling, the impurities which rise to the surface are removed and the solution concentrated in another vessel, and eventually crystallised in lead-lined tanks.

Brown sugar of lead is prepared in a similar manner by substituting crude acetic acid (pyroligneous acid) for the purer acid. If excess of litharge be used basic acetates are produced.

Pure lead acetate forms white crystals, which have a sweet taste and a slight acid reaction. The salt effloresces in the air, and dissolves in about twice its weight of cold water.

White lead acetate usually contains about 99 per cent. of the crystallised salt ; the *brown* variety only contains about 90 per cent.

Solutions of lead acetate absorb carbon dioxide from the air, and turn milky owing to the formation of lead carbonate.

Lead acetate is used for the preparation of alum mordants, &c., and in the preparation of chrome yellow and other pigments.
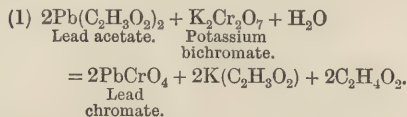
LEAD CARBONATE, $PbCO_3$, occurs native as *cerussite.* It is formed as a white precipitate when ammonium carbonate is added to a solution of lead nitrate. The carbonates of potassium and sodium form basic carbonates varying in composition according to the temperature and concentration of the solutions. A basic salt having the usual composition $2PbCO_3$. $Pb(OH)_2$ is known as *white lead.*
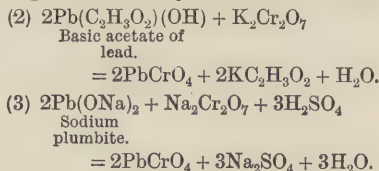
Preparation of White Lead.—In the so-called *Dutch process* rolls of sheet lead are placed in earthenware vessels containing a little acetic acid, and surrounded by fermenting tan. The basic acetate formed by the action of the acid on the metal is converted into carbonate by the carbon dioxide liberated from the fermenting organic matter. Acetic acid is thus reproduced and this continues until all the lead is converted into basic lead carbonate. Another process consists in dissolving litharge in acetic acid and then saturating the solution with carbon dioxide.

Properties of White Lead.—This substance is a white heavy powder which is much used for mixing with oil in the preparation of paint. The greater the density of the sample the greater its covering power. Paint containing white lead turns dark in presence of hydrogen sulphide, lead sulphide being formed.

LEAD CHROMATE or CHROME YELLOW, $PbCrO_4$. Chromate of lead occurs native, and is manufactured in large quantities as a pigment by precipitating the solution of a lead salt (acetate or nitrate of lead) with bichromate of potassium or sodium :—

(1) $2Pb(C_2H_3O_2)_2 + K_2Cr_2O_7 + H_2O$
　　Lead acetate.　　Potassium
　　　　　　　　　　bichromate.

$= 2PbCrO_4 + 2K(C_2H_3O_2) + 2C_2H_4O_2.$
　　Lead
　　chromate.

The compound can also be produced from a basic lead salt or from an alkaline plumbite (compound of lead hydroxide and an alkali).

(2) $2Pb(C_2H_3O_2)(OH) + K_2Cr_2O_7$
　　Basic acetate of
　　　lead.

$= 2PbCrO_4 + 2KC_2H_3O_2 + H_2O.$

(3) $2Pb(ONa)_2 + Na_2Cr_2O_7 + 3H_2SO_4$
　　Sodium
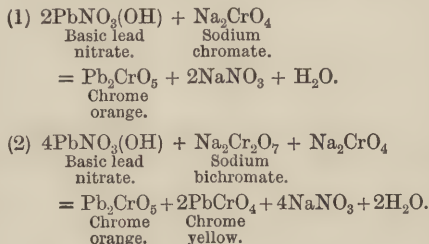　　plumbite.

$= 2PbCrO_4 + 3Na_2SO_4 + 3H_2O.$

Chrome yellow forms an orange-yellow powder, and is quite insoluble in water and other neutral solvents, but dissolves readily in nitric acid and in caustic potash or soda ; the latter reagents, however, convert it first into a basic lead chromate. (*v.* Chrome Orange).

Chromate of lead is used as an oxidising agent in the laboratory, and has also been recommended as such for the production of aniline black by oxidising the aniline in the fibre.

Chrome yellow is produced in dyeing by first impregnating the fibre with a lead salt, and then passing the material through a solution of a bichromate. The processes are precisely similar to those which occur in mordanting and dyeing with the mordant colours ; the lead salt plays the *rôle* of the mordant and the bichromate acts as the dyestuff. The analogy goes still further, inasmuch as the dyestuff possesses a distinct chromophor " Cr," and—in the form of free chromic acid, H_2CrO_4—the auxochromous group (OH). Finally, lead is not the only mordant for the bichromate dyestuff, although by far the best, since soluble barium salts produce a similar chrome yellow, $BaCrO_4$.

CHROME ORANGE.—This substance consists of a mixture of normal lead chromate (chrome yellow) and basic lead chromate, Pb_2CrO_5. It is also used as a pigment. It is produced by precipitating the solution of a basic lead salt with sodium bichromate or chromate ; the colour appears the redder the more alkaline the mixture is—*i.e.*, the less chrome yellow the ultimate colour contains.

(1) $2PbNO_3(OH) + Na_2CrO_4$
    Basic lead   Sodium
    nitrate.   chromate.

    $= Pb_2CrO_5 + 2NaNO_3 + H_2O.$
        Chrome
        orange.

(2) $4PbNO_3(OH) + Na_2Cr_2O_7 + Na_2CrO_4$
    Basic lead   Sodium
    nitrate.   bichromate.

    $= Pb_2CrO_5 + 2PbCrO_4 + 4NaNO_3 + 2H_2O.$
      Chrome   Chrome
      orange.   yellow.

Chrome yellow may be converted into chrome orange by the action of alkalies or lime water ; it is in this way that chrome orange is produced in dyeing. Chrome orange forms an orange to red powder ; it resembles chrome yellow in its chemical properties. Chrome yellow and orange are poisonous.

Dr. Carry of Lyons observed a series of poisoning cases amongst women engaged in reeling yellow or orange-coloured yarns. All the symptoms indicated lead poisoning. Messrs. Schulz and Weyl found the ashes of these yarns contained 95 and 77 per cent. of lead chromate.

Tests for Lead Chromate.—Warm soda lye removes chrome yellow and orange completely, and on the addition of ammonium sulphide to the solution a black precipitate results. The latter is soluble in nitric acid. The concentrated soda solution produces, with sulphuric acid and alcohol, a white precipitate of lead sulphate, which is turned black with sulphuretted hydrogen.

LEAD HYDROXIDE, $Pb(OH)_2$, is precipitated by caustic alkalies from solutions of lead salts as a voluminous white mass.

The precipitate is insoluble in ammonia, but excess of caustic potash or soda dissolves it with formation of *plumbites*. The hydroxide is slightly soluble in water, to which it imparts an alkaline reaction.

LEAD NITRATE, $Pb(NO_3)_2$, is obtained by dissolving lead or oxide of lead (litharge) in hot dilute nitric acid. The salt crystallises in regular octahedra, which dissolve in 8 parts of cold water. Lead nitrate is sold in the form of white lumps, and often contains copper as an impurity.

Lead nitrate is used in the preparation of orange and yellow colours in cotton dyeing and printing.

A solution of the *basic nitrate of lead*, $Pb(NO_3)(OH)$, is prepared by boiling a solution of the normal salt with the calculated amount of litharge. This substance is employed in the weighting of silk.

LEAD OXIDES. LEAD MONOXIDE, PbO, is prepared by heating lead in air with constant stirring. It has a brownish-yellow colour, and, when ground, the powder is termed *massicot*. If the oxidation of lead be carried out at a higher temperature, so that the oxide formed is melted, orange-coloured scaly crystals, called *litharge*, are formed.

Properties.—Lead oxide has a strong basic character. With water it gradually forms lead hydrate, which goes into solution slowly. It is soluble in hot solutions of caustic potash and soda. Acetic acid and nitric acid also dissolve it. It is used in the preparation of lead acetate, nitrate, and of lead plaster.

LEAD TETROXIDE, Pb_3O_4. *Red lead Minium.* Is a compound of lead monoxide and lead dioxide ($2PbO + PbO_2$).

Red lead is prepared by heating *massicot* in the air at a low temperature until it becomes of a bright red colour. It is insoluble in water. Dilute nitric acid dissolves out the lead monoxide, and leaves the dioxide unattacked. It is soluble in glacial acetic acid, forming a mixture of acetates.

Red lead is used as a pigment in glass making, as a paint to prevent iron from rusting, and as a cement for water and steam joints.

LEAD PEROXIDE, PbO_2. *Lead dioxide* is a brown powder which remains when red lead is treated with nitric acid. On heating, it is reduced to the tetroxide. It is not readily attacked by acids, and does not form salts with them. Lead dioxide dissolves in hot solutions of caustic soda or potash, forming sodium and potassium plumbates (Na_2PbO_3 and K_2PbO_3). These compounds and also lead dioxide are strong oxidising agents.

LEAD SALTS are generally colourless. They are poisonous, and those which dissolve in water have an acid reaction and a metallic taste. Lead hydrate is precipitated from

solutions of lead salts by caustic alkalies, an excess of the latter (excepting ammonia) redissolving the hydroxide. Carbonate of soda precipitates basic carbonate of lead. Hydrochloric acid or chlorides form a white precipitate of lead chloride, which is soluble in a large excess of cold water, and readily in boiling water.

On the addition of sulphuric acid or solutions of sulphates to lead salts, white insoluble lead sulphate is precipitated. Chromates form chromate of lead (chrome yellow), which is easily soluble in caustic potash or soda. Sulphuretted hydrogen or ammonium sulphide forms black sulphide of lead (PbS), which is insoluble in acids, alkalies, and alkaline sulphides ; hot dilute nitric acid dissolves the sulphide forming lead nitrate, but concentrated acid oxidises it to lead sulphate.

LEAD SULPHATE, $PbSO_4$, is a white crystalline substance, insoluble in water. Hot HCl converts it into chloride. Caustic alkalies dissolve lead sulphate.

LEATHER BLACK C, T (M.). Colour used in dyeing leather tanned by the chrome process.

LEATHER BROWN v. BISMARCK BROWN.

LEATHER BROWN (O.). An azo dye of a basic character.

Metaphenylene diamine $\Big\langle$ *Amido paraacetanilide.*
Amido paraacetanilide.

1890. Blackish powder, soluble in water with a brown colour. In concentrated H_2SO_4, brown solution ; on dilution, becomes redder.

Application.—A basic dye. Specially suitable for *leather* and *jute*.

LEATHER BROWN (M.) v. PHOSPHINE.

LEATHER YELLOW (M.) v. PHOSPHINE.

LEMON JUICE v. LIME JUICE.

LIGHT, ACTION OF, UPON DYES v. DYES.

LIGHT BLUE v. DIPHENYLAMINE BLUE.

LIGHT GREEN v. METHYL GREEN.

LIGHT GREEN S F BLUE SHADE (B.) v. ACID GREEN (By.).

LIGHT GREEN S F YELLOW SHADE (B.) v. ACID GREEN (By.).

LIGNOCELLULOSE v. COTTON.

LIGNOROSIN v. CALCIUM LIGNOSULPHONATE.

LIME JUICE, LEMON JUICE. These substances are used by calico printers, chiefly as resists for iron and alumina mordants ; the bases of these mordants being quite soluble in citric acid are in its presence thus prevented from attaching themselves to the fibre. Lime juice is used also for precipitating *carthamin*, the red colouring matter of safflower, from its alkaline solutions.

Such juices are, however, liable to admixture with tartaric, sulphuric, and oxalic acids, sulphates, chlorides, iron, &c., which must be tested for (v. CITRIC ACID).

Lime juice, if pure, can be used in almost every case as a cheap substitute for crystallised citric acid. It is a dark coloured liquid of oily consistency, and contains 26 to 36 per cent. of citric acid.

Determination of Citric Acid.—The following method suggested by R. Warrington may be used if mineral acids only are present ; oxalic or tartaric acid would render it inapplicable :—20 c.c. of diluted lime juice or about 3 c.c. of the concentrated lime juice accurately weighed and then diluted, are exactly neutralised with caustic soda. The solution is brought to a bulk of about 50 c.c., and heated to boiling on the sand bath, when so much of a solution of calcium chlorate is added as is known to be rather more than equivalent to the total organic acid present. The whole is boiled for half an hour, and the precipitate then collected and washed with hot water. The filtrate and washings are concentrated to about 10 c.c., the solution being finally neutralised with a drop of ammonia if it has become acid. The second precipitate thus obtained is collected on a very small filter, the filtrate being employed to transfer it, and the washing with hot water being reduced as much as possible. The precipitates with their filters are then burnt at a red heat, and the neutralising power of the ash ascertained by treatment with standard hydrochloric acid. Each c.c. of $\frac{N}{1}$ acid used = $0\cdot070$ grm. of crystallised citric acid ($C_6H_8O_7 + H_2O$).

LINEN v. FLAX.

LINSEED OIL is obtained from the seeds of flax, *Linum usitatissimum.* It has a light yellow, or if obtained by hot pressing, a brownish-yellow colour, and a peculiar smell and taste. The specific gravity at 15° C. is $0\cdot930$ to $0\cdot939$; it solidifies slowly at $-16°$ to $-27°$. In the air it absorbs oxygen, and soon becomes rancid and thick, drying in thin layers to a neutral substance which is insoluble in ether. It is adulterated with fish oil, rape oil, hempseed oil, and cameline oil.

Linseed oil is chiefly used by painters on account of its property of drying and forming a varnish. For the same reason it is used in cotton velvet dyeing. Prussian blue and other colours in a finely-ground state with linseed oil are painted on the velvet with brushes, in order to give the fabric colour and a fine gloss.

LITMUS is produced from orchella weed by a process which differs somewhat from that adopted in the manufacture of orchil. The commercial article is sold in small granulated masses, which contain much mineral matter — usually plaster of Paris. It is not now used in dyeing, but is employed

as an indicator in analytical chemistry, since its solution is very readily turned blue or red by traces of alkali or acid respectively (v. also INDICATORS).

LOGWOOD.—This, the most important of the natural dyewoods, was introduced into Europe by the Spaniards shortly after the discovery of America (about 1500). It does not, however, appear to have been used in England until 1570 to 1580, since in 1581, "a few years after its introduction," its use was prohibited by Act of Parliament, "because the colours produced from it were of a fugacious character." The wood, however, continued in use, surreptitiously, under the name of "blackwood," until the prohibition was removed in 1673, the preamble of the Act legalising its use, stating that "the ingenious industry of modern times hath taught the dyers of England the art of fixing the colours made of logwood, *alias* blackwood, so as that, by experience, they are found as lasting as the colours made with any sort of dyeing wood whatever."*

Origin.—Logwood is the product of a large, leguminous, and rapidly growing tree, the botanical name of which is *Hæmatoxylon Campechianum.* Being obtained in the first instance from the Bay of Campeachy, it was long known as "Campeachy wood," but the amount imported from that district is now very small, the bulk of the supply coming from Jamaica and Honduras, with smaller importations from St. Domingo, Cuba, Laguna, Yucatan, &c. The annual consumption of logwood in the United Kingdom at the present time is probably about 60,000 tons.

When first cut down the wood has a yellowish-brown colour, but on exposure to the air it gradually develops a more or less superficial rich brownish-red colour. It is imported into this country in the form of rough logs, from which the outer bark has been removed, but before being employed by the dyer the wood is reduced to small chips, or rasped to powder, these products being distinguished respectively as "chipped logwood" and "rasped" or "ground logwood." Many liquid and solid "extracts of logwood" are also employed.

COLOURING PRINCIPLE AND COLOURING MATTER OF LOGWOOD.

The colouring matter of logwood was first investigated by Chevreul in 1811, who obtained from it two bodies, the chief being a yellowish white crystalline body, which on exposure to air in the presence of a trace of ammonia rapidly darkens in colour. To this body Erdmann later gave the name hæmatoxylin, by which it is now known.

* "Philosophy of Permanent Colours," Bancroft.

Hæmatoxylin.—It is uncertain whether this substance exists in the growing wood, but it is certainly present in large quantities in the freshly chipped or ground wood, of which a good sample of logwood may contain 8 to 10 per cent. It may be obtained by extracting freshly cut logwood with water containing a little sulphurous acid, and crystallising from the solution thus produced; or more readily by extracting the dry freshly cut wood with ether, evaporating to a syrup, then adding a little water, and allowing the solution to stand until hæmatoxylin crystallises out.

When pure it forms white prismatic crystals, having the composition $C_{16}H_{14}O_6$. It is only slightly soluble in cold water, but dissolves readily in hot water, alcohol, ether, or carbon disulphide. It cannot be volatilised without decomposition. When fused with caustic alkali it yields *pyrogallic acid* ($C_6H_3(OH)_3$), a derivative of benzene. It acts as a feeble acid, forming salts with bases, but if oxidising influences are excluded, it is absolutely devoid of dyeing power, its metallic derivatives being colourless. It absorbs oxygen with great avidity, particularly in presence of alkali, being converted into the brownish-red colouring matter *hæmatein.*

Hæmatoxylin is thus the *colouring principle* of logwood, the *colouring matter*, hæmatein, being produced from it by oxidation.

Hæmatein has the composition $C_{16}H_{12}O_6$. It forms brownish-red crystals, which possess a green metallic lustre, and is most readily prepared by exposing to the atmosphere a solution of hæmatoxylin rendered slightly alkaline with ammonia. Under these conditions a deposit of hæmateate of ammonia is gradually formed, which is decomposed by, and crystallised from, dilute acetic acid.

Hæmatein is almost insoluble in cold water, but more easily soluble in hot water or alcohol, giving a yellow or brown solution. It readily forms salts with bases, its combinations with soda, potash, or ammonia being easily soluble, with a fine purple colour. In combination with the heavy metals, it produces strongly-coloured insoluble salts, upon the formation of which its value as a dyestuff depends. Solutions of the alkaline hæmateates undergo atmospheric oxidation with great ease; useless brown, resinous bodies being produced, which like hæmatoxylin and hæmatein, are capable of forming salts with metals.

The green bronzy appearance often seen on logwood chips is not due to hæmatein, but to its ammonium (or other alkali) compound.

The colour-producing substance in logwood may thus exist in three different states of oxidation, viz.:—(1) Hæmatoxylin, the colour-

ing principle; (2) hæmatein, the colouring matter, which is alone of practical use; and (3) the useless brown resinous oxidation product of hæmatein.

THE "AGEING" OF LOGWOOD.—This process, which is sometimes known as "curing," "maturing," or "getting up" of the wood, has for its object the production of the maximum amount of hæmatein.

It is carried out as follows:—The ground or chipped wood is spread out upon a wooden floor in layers about 12 inches in thickness, a certain amount of water (25 to 30 per cent. of the weight of wood) being sprinkled thereon. Several such layers being placed on each other, the whole mass, which may be 4 or 5 feet high, is well mixed together by means of wooden spades. Another method is to mix successive quantities of the wood with the requisite amount of water in large revolving drums, subsequently spreading out as before.

After standing for some time a slight heating of the mass of wet wood takes place, and the heaps are frequently turned over and remixed, in order to prevent undue elevation of temperature and to equalise the action. The operation lasts altogether for several weeks, the time varying according to the state of the atmosphere, and being shorter in summer than in the winter months. The process requires the exercise of great care and judgment, since excessive fermentation may take place in the course of a few hours under certain atmospheric conditions, this resulting in partial or total destruction of the colouring matter. Wood in this condition is technically known as "over-aged," or "burnt," and is useless for dyeing purposes.

During the progress of the process the wood gradually changes in colour from yellowish-brown to rich reddish-brown or brownish-crimson, but if over-aged the red colour entirely disappears, the wood appearing dark brown. In order to accelerate the operation, a small amount of alkali (ammonia), or of some highly nitrogenous matter (e.g., glue) is sometimes added to the water used in damping the wood, but this practice is dangerous because of the greater liability to "over-ageing" which it introduces.

With regard to the actual changes which occur during the ageing process, Hummel considers that the action consists essentially in the oxidisation of hæmatoxylin into hæmatein, and not, as has been frequently stated, in the decomposition of a glucoside. This view is rendered highly probable by the fact that in dyeing properties freshly-cut logwood behaves exactly like hæmatoxylin, and properly aged wood corresponds equally well with hæmatein.

Undoubtedly, a fermentation occurs during ageing which will modify certain of the extractive matters other than hæmatoxylin,

and the production of ammonia during this fermentation materially assists the production of hæmatein, since the hæmatoxylin oxidises much more readily in presence of alkali.

It is evident that the correctness of Hummel's view that "ageing" consists essentially in an oxidisation, is becoming more and more recognised, since patents have been taken out for accelerating the process by the use of chlorine, or of compressed oxygen, both of which, of course, act simply as oxidising agents, and would have an injurious effect if the ageing process consisted in decomposing a glucoside.

It is generally considered the "ageing" of logwood is a necessary preliminary to its employment in dyeing, but this is certainly incorrect, since the development of the colouring matter may, in many cases, readily be brought about during the dyeing operation itself. The extensive and rapidly increasing use of extracts of logwood, which are prepared from the freshly-cut wood, is, indeed, in itself a proof that for many purposes ageing is not essential.

Gardner has shown that there are four distinct methods by means of which the dyeing power of the freshly-cut wood may be developed, viz. :—

(1) Ageing in the ordinary way—i.e., exposing the wood to air in a moist condition.

(2) Ageing quickly by means of compressed oxygen, hydrogen peroxide, chlorine, or other suitable oxidising agent.

(3) Ageing in the dye-bath by adding hydrogen peroxide or other suitable oxidising agent.

(4) Ageing in the dye-bath by mordanting previously with an oxidising mordant, such as chromic acid.

Selection between these alternative processes resolves itself into a consideration of their relative economy and efficiency, and the retention of the ordinary ageing process is more a matter of convenience than of necessity. The change from hæmatoxylin to hæmatein is never complete in the ordinary commercial aged logwood, which thus contains a variable mixture of the two. Aged logwood also contains from 25 to 35 per cent. of moisture.

LOGWOOD EXTRACTS.

Two principal methods are in use for the manufacture of logwood extracts on the large scale, these being known respectively as the French and the American systems. In the former, the wood is extracted in open vessels with warm or boiling water, while in the American system closed vessels are employed, and the extraction takes place under a steam pressure of from 15 lbs. to 30 lbs. per square

inch. In both processes the dilute extract is subsequently concentrated by evaporation in a partial vacuum, and is sold either as "logwood liquor" at about 15° Tw., "logwood extract," which is usually about 51° Tw., or in the solid state as "solid logwood extract."

The extract is usually prepared from "unaged" or freshly-cut logwood, and this is rational for several reasons. In the first place, hæmatoxylin is much more soluble than hæmatein, and therefore the colouring matter is more easily extracted in the former condition; secondly, it is inevitable that some oxidation occurs during extraction and concentration, and this leads to a corresponding destruction of colouring matter, if the latter has already, in the ageing process, been converted into hæmatein.

In order to prepare extracts in which the colouring matter is in the same condition as in aged wood, the colouring matter should be very carefully oxidised after extraction and evaporation. Products of this type are sold under such names as " oxidised logwood extract," "hæmatein," "logwood extract for wool," &c., and the oxidation is brought about either by exposure to air, or by addition of some oxidising agents of which many have been proposed, viz. :—Chlorine gas, oxides of nitrogen, hydrogen peroxide, potassium chlorate, nitrate, permanganate, and ferricyanide, bleaching powder, &c., &c.

Valuation of Logwood and Logwood Extracts.—Since logwood contains a variable amount of coloured extractive substances other than colouring matter, it is evidently impossible to estimate the amount of the latter by any process based upon the colour of the logwood decoction obtained by boiling with water. There are, however, several colorimetric tests for valuing logwood, which are based upon the fact that a solution of alum, or other metallic salt, gradually develops a blue or purple colour in a logwood decoction, the intensity of which is proportional to the amount of colouring matter present.

Rawson * proceeds as follows :—10 grms. of logwood, or an equivalent amount of extract, are completely extracted by alcohol, and the solution diluted to 1 litre; 10 c.c. of this solution are further diluted with 90 c.c. of alcohol; then 5 c.c. of the dilute solution are put into a Nessler glass; 5 c.c. of a 1 per cent. solution of alum is added, and the solution made up to the mark with distilled water. The colour produced (which develops gradually) is compared with a standard sample treated in an exactly similar manner, more of the weaker solution being added, until the intensity of colour in the two solutions is equal. The relative value

of the two samples will then be in inverse proportion to the volumes of the two liquids.

Trimble * had previously proposed a similar process in which copper sulphate is employed.

The most reliable method of estimating the value of samples of logwood, or logwood extracts, is by means of comparative dye trials, carried out under the exact conditions under which the dye is to be practically employed. It is essential that strict attention be paid to the latter point, because the practical value of any sample depends largely upon the process used in applying it. For instance, in the case of two samples of wood containing the same total amount of colouring matter, the latter may consist in one sample of hæmatoxylin, and in the other of hæmatein, and, if dyed on an oxidising mordant (e.g., chromic acid), the former would give a much superior (brighter) colour, whereas, on a non-oxidising mordant (e.g., chromium fluoride), the latter would give much the best result.

The practical value for a particular purpose, represented by the condition of the colouring matter, may thus be very different from the theoretical value, as measured by the total amount of colouring matter present.

In the case of logwood extracts, these remarks apply with even greater force, because not only is the degree of oxidation of the colouring matter very variable, but their value may be largely influenced by the presence of impurities. Admixture with such bodies as bark extract, molasses, glucose, dextrin, tannin extracts, &c., is largely practised, and is by no means easy of detection. Inorganic adulterants, such as salt, sodium sulphate, or chalk are also of frequent occurrence, but the detection and estimation of these offers no difficulties. Even in the case of unadulterated extracts a mere determination of the specific gravity gives no indication of the amount of colouring matter present, on account of the variable amount of other extractive matters which may be present.

The nature of the impurities may have an important influence upon the suitability of any sample for a special purpose. Thus an extract to which 20 per cent. of chestnut extract has been added would be much inferior for wool dyeing to one containing an equal amount of colouring matter reduced with 20 per cent. molasses, because tannin matters tend to give the wool a harsh unpleasant feel, and are thus injurious. For use in the black dyeing of cotton, however, the two extracts would be reversed in value, because the tannin, combining with the iron used as mordant, would help to intensify the black.

* Manual of Dyeing, Knecht, Rawson, and Lowenthal, p. 812.

* Journ. Soc. Dyers and Col., 1885, p. 92.

A perfectly satisfactory method of analysis should, therefore, indicate the following points :—

(1) Amount of hæmatoxylin ; (2) amount of hæmatein ; (3) character and approximate amount of impurities.

There is, however, at present no analytical method in vogue which satisfactorily determines these points, and the most reliable results are obtained by carefully conducted comparative dye trials made under the conditions of practical work.

Zubelin [*] proceeds as follows :—Standard solutions are prepared containing 5 grms. extract 51° Tw. per litre, having the following composition :—

(1) Colouring matter entirely unoxidised (hæmatoxylin).

(2) Colouring matter entirely oxidised (hæmatein).

(3) Equal parts of hæmatoxylin and hæmatein.

(4) Four grms. hæmatoxylin paste and 1 grm. sumac.

(5) Same as No. 1, mixed with 0·5 per cent. chalk.

With these various solutions dye-baths are made up containing 40 c.c. of the solution and 400 c.c. distilled water, and in each, 10 grms. of wool previously mordanted with 3 per cent. bichromate of potash and 3 per cent. tartaric acid is dyed.

The results obtained will be as follows :—

(1) Bright bluish colour.

(2) Much deeper than 1, approaching black.

(3) Colour intermediate between 1 and 2.

(4) Paler than 1.

(5) About equal to 3.

A similar piece of wool is dyed at the same time with solutions of the extracts under examination made up to the same strength as the standard extracts—viz., 5 grms. 51° Tw. per litre, and the colours thus obtained are compared with the above. It is thus easy to determine when the extracts are partially or completely oxidised. An oxidised adulterated extract may, however, give a similar colour to an unoxidised pure extract, and the following further trials are therefore necessary :—

Wool is mordanted with—

    10 per cent. alum.

    $2\frac{1}{2}$,,   potassium bichromate.

    $2\frac{1}{2}$,,   copper sulphate.

    $2\frac{1}{2}$,,   tartaric acid.

Patterns thus mordanted are dyed as before, but using only 20 c.c. of the various extracts and 400 c.c. water. The results obtained are very different to those in the first set of experiments—

(1) Deep blue.

(2) Grey and much paler than 1, 3, 4, or 5.

(3) Duller than 1.

    * *Bull. Soc. Ind. Mulhouse,* 1898, p. 257.

(4) Similar to 1, but somewhat paler.

(5) Similar to 3.

In the case of the two extracts which may appear similar in the first set of experiments, but which differ in that one is an unoxidised extract and the other an adulterated oxidised extract, very different results will be obtained on this composite mordant, the pure unoxidised extract giving much the deeper and brighter colour.

By making additional experiments on cotton, further information or corroboration regarding the degree of oxidation of the samples may be obtained, as will be seen from the following notes :—

Additional standard solutions are prepared as follows :—

(6) As 1.

(7) As 2.

(8) As 2, diluted 20 per cent.

(9) As 4.

(10) As 4, with enough chalk to neutralise the tannic acid.

(11) As 5.

Cotton hanks are dyed in solutions containing 100 c.c. of these extracts diluted to 400 c.c., commencing at 60° to 70° C., and allowing gradually to cool during $1\frac{1}{2}$ hour. After being well shaken out, each hank is immersed for five minutes in a bath containing 3 per cent. of copper sulphate.

The dyed patterns exhibit the following appearances :—

(6) Light grey.

(7) Blue-black.

(8) Between 6 and 7.

(9) Poor light dull colour.

(10) Darker than 9, but paler than 8.

(11) Darker than 6, but paler than 7 and 8.

The reason for the poor results obtained in (9) is that hæmatein is not well attracted by cotton in presence of tannic acid in solution. Extracts containing tannic acid may be further recognised by the peculiar reddish-grey shade they produce.

Logwood extracts containing *molasses and dextrin* have an abundant sediment, and in the former case also an increased residue of ash. Pure extracts, however, often yield up to 8 per cent. ash. Some sugar molasses yield 8 per cent. of ash, others give 20 per cent. ash. Suppose the following extract mixture has been made :—

		Per cent. Ash.	Grms. Ash.
100 parts logwood extract of	6·40	.	6·40
25 ,, molasses ,,	11·20	.	2·80
75 ,, quebracho ,,	1·22	.	0·91

200 grms. mixture contain, therefore, 10·11 grms. ash, and the extract mixture contains 5·05 per cent. ash—that is, 1 per cent. less than the original pure extract.

If the same mixture is made with an

extract whose ash is less and can be assumed as normal, for instance :—

	Per cent. Ash.		Grms. Ash.
100 parts logwood extract of	2·85	.	2·85
25 ,, molasses ,,	11·20	.	2·80
75 ,, quebracho ,,	1·22	.	0·91

200 grms. mixture contain, therefore, 6·56 grms. ash, or the extract mixture contains 3·28 per cent. ash—that is, notwithstanding the addition of 25 per cent. of a substance very rich in ash, the percentage of ash has not much increased. The amount (3·28) is not at all high, and the extract would therefore, if judged according to the percentage of ash alone, have to pass as a normally pure extract.

Determination of Molasses.—5 grms. of extract are dried at 100° C. and extracted with absolute alcohol until a small quantity of the alcohol with sodium aluminate gives no longer any reaction for hemateïn; this alcoholic extract is preserved. In the residue, besides the substances insoluble in alcohol which occur in extracts, is contained the sugar of the molasses and dextrin.

As a normal extract may contain 0·5 per cent. grape sugar, but never cane sugar, the detection of the latter in the residue after the alcoholic extraction is the surest proof of the presence of molasses. Any surplus above 1 per cent. grape sugar is a proof of added grape sugar.

Chestnut extract is detected as follows :— The alcoholic extract is evaporated to dryness, the residue dried at 100° C., the mass obtained extracted with ether, and the weight of the etherial extract ascertained, the portion which is insoluble in ether being separately weighed. The comparison of these weights of etherial and alcoholic extracts with those obtained by an examination of a pure logwood extract carried out in the same manner shows whether chestnut extract has been added. Chestnut extract is practically insoluble in ether, while it is readily soluble in alcohol; therefore less ether extract and more alcoholic extract will be found in adulterated than in pure extracts. The products of the two extracts which are soluble in alcohol and ether must equally dye similar weights of material if they have the same composition. By comparative dye-trials with the solutions made from these residues, the value of the extracts can be accurately determined to 1 to 2 per cent.

A direct comparison of different extracts, without previously dissolving in ether and alcohol. will not, in case tannin matters have been added, allow of an exact estimation of the extract.

The addition of Glauber's salt to the extract is injurious. If ferrous sulphate be used in dyeing with such adulterated extract, uneven dyeing may result, owing to the formation of ferric sulphate on the fibre. In the production of steam blacks on cotton with acetic acid and chromium acetate with such extract, sodium acetate is formed, which prevents the complete oxidation of the colour in the steaming apparatus.

The Detection and Estimation of Sugar.— Schweissinger [*] dissolves about 4 grms. of the extract in 50 c.c. water, adds 10 c.c. basic lead acetate, agitates the mixture well, and, after standing, filters through a dry filter. So much of the liquid is allowed to run through that it can be polarised at once in a 100 mm. tube. Filtrates from pure extracts deflect the plane of polarisation either very slightly or not at all, while if sugar is present the solution will be dextro-rotatory. Further, 25 c.c. of the filtrate is mixed with so much hydrochloric acid that the lead is precipitated as chloride, and about 0·5 grm. of acid remains in excess. The acid liquid is heated on a reflux condenser for half an hour, and allowed to cool. The crystals of lead chloride are disregarded, and the liquid is neutralised with sodium carbonate, made up to 50 c.c., filtered through a dry filter, and an aliquot portion titrated exactly, or precipitated with an excess of Fehling's solution.

The *reaction* of a logwood extract is recognised from the colour of its solution. Neutral solutions are of a deep red; alkaline solution, blue-red; acid solutions, light yellow if unfermented, orange-yellow if fermented. In extracts with an addition of tannin, the reaction is constantly acid, and, in contrast with the naturally acid extracts prepared under pressure, the colour is not immediately changed into the neutral red on diluting with water containing lime, or on shaking and heating with a small quantity of calcium carbonate.

Another characteristic test is furnished by the reaction with stannous chloride. To an extract solution of about 5° Tw. a solution of chloride of tin is added. In fermented extracts the precipitate is dark brown, in unfermented, light yellow; in extracts containing tannin there is a dirty, yellowish precipitate. To recognise an addition of tannin the ammonium sulphide reaction is useful. If to a solution of 5 grms. of dry extract in 1 litre water, one-third of its volume of ammonium sulphide is added, pure extracts show a weak brown and flaky precipitate, and the solution assumes a dark colour, while in extracts containing tannin the colour of the solution becomes lighter, with the immediate formation of a dense light grey milky precipitate. In a solution of about 1 grm. per litre, pure extracts only show a strong turbidity, which in a short time aggregates in larger light flakes.

* *Chemical News*, vol. lx., p. 49.

Application of Logwood.—Logwood is a mordant dye and gives, with various metallic mordants, the following colours :—

Chromium,	.	Blue and black.
Iron,	. .	Grey and black.
Copper,	. .	Olive and greenish-black.
Aluminium,	.	Dull violet-blue.
Tin,	. . .	Purplish-blue.
Zinc,	. . .	Purplish-brown.
Uranium,	.	Bluish-grey.
Nickel,	. .	Drab.

The principal use of logwood is for the production of blacks on all fibres, although it is also largely employed in conjunction with other colouring matters—fustic, madder, and the alizarin dyes—for producing greys, drabs, olives, &c. ; in fact, it is the most generally used of all dyestuffs.

Logwood is also an extremely cheap dye. If the amount of moisture in a sample of wood, sold at £8 per ton, is 33 per cent., the amount of colouring matter may, at a low estimate, be taken at 5 per cent. On this basis, the price of the pure hæmateïn in the logwood is about 1s. 5d. per lb., and in dyeing power it is equal to ten times its weight of alizarin black, or to twice its weight of an acid coal-tar black.

In computing the actual cost of the dyed colours, it is, however, necessary to take into account the cost of the mordant, labour, steam, &c., required, which, being usually greater in the case of logwood than in dyeing with the acid blacks, thus reduces the cost of black dyed with some of the latter slightly below that of a logwood dyed black.

In *wool dyeing* logwood blacks are dyed in conjunction with either chromium or iron mordants, the dyes being known as " chrome blacks " and " copperas blacks " respectively. They may be distinguished by spotting a piece of the dyed cloth with a drop of sulphuric acid, 100° Tw., which produces an olive-brown spot with chrome blacks and a crimson-red spot with copperas blacks.

In *silk* and in *cotton dyeing* logwood extract is largely used for blacks, the fibre being previously mordanted with iron and tannin.

LONDON BLUE EXTRA (Br. S. & Sp.) *v.* Soluble Blue.

" LO KAO " or " CHINESE GREEN " is the only example of a natural green dyestuff. It was first brought to Europe about 100 years ago, and it was at first thought that the Chinese had succeeded in fixing the green colouring matter of grass upon the silk, but later it was found that the dye was produced by a complicated process from the sap of *Rhamnus utilis* and *Rhamnus chlorophorus*, and is somewhat allied to indigo-blue.

When first imported, this dyestuff was sold for as much as £10 per lb. weight, but it is now of purely historical interest.

LUBRICATING OILS. Oils of this class have for their object the reduction of friction between surfaces. The purpose for which it is intended must always be considered when selecting a lubricating oil.

The following determinations will be found useful in forming an opinion as to the suitability of an oil for lubricating purposes :—

(1) The specific gravity at 15° C. and at 100° C.

(2) The viscosity or " body " of the oil at the same temperature at which it will be employed.

(3) The amount of mineral and fatty acids.

(4) The percentage of mineral and fatty oils (saponifiable matter).

(5) The volatility or loss in weight which the oil undergoes when heated for twelve hours at the temperature to which it will be exposed when in use.

(6) The tendency of the oil to act on the particular metals with which it will come in contact.

(7) The presence of mineral matter or soap.

(8) The liability of the oil to gum.

(9) The flashing point or the temperature at which the oil gives off inflammable vapours.

(10) The temperature at which the oil solidifies.

Fatty oils decompose at high temperatures, forming free fatty acids which attack metals, hence mineral oils are preferable for cylinders.

Sperm, neatsfoot, tallow, and lard are the most used animal oils, and olive, palm, rape, and cottonseed are the best vegetable lubricating oils.

As resin oils are liable to gum, their absence should be demonstrated.

Purified mineral oils of the necessary viscosity should be used when possible.

Analysis.—The *specific gravity* at 15° C. is taken by means of the specific gravity bottle, and at 100° C. with the aid of a Sprengel's tube (*v.* Soap, Analysis of Fatty Matter in).

The specific gravity of lubricating oils at 15° C. ranges from 0·850 to 0·925.

The *viscosity* or " body " is most accurately determined by means of Redwood's viscometer. In the absence of this instrument a good idea of the viscosity may be obtained by filling a 50 c.c. burette with the oil at 15° C. and counting the number of seconds required by the outflow of 50 c.c. of the oil. This number may then be compared with the figures obtained by testing other samples in a similar manner or with the numbers given by a refined rape oil. In the latter case the number of seconds required is taken as a standard and the viscosity reckoned as 100.

If rape oil require 535 seconds, the viscosity of any other oil is (if x = number of seconds)

$$\frac{x \times 100}{535}.$$

If the oil to be tested differs in specific gravity to that of rape oil—viz., 0·915 at 15°5—then the formula becomes

$$\frac{x \times 100 \times sp.\ gr.}{535 \times ·915}$$

Free mineral acid is sometimes present in oils. The quantity should be very small, or bearings, &c., will be corroded. The amount is determined by weighing off about 25 grms. into a dry 200 c.c. flask. About 150 c.c. of boiling water are added to the oil and the flask placed in a bath of boiling water. The contents of the flask are shaken repeatedly for half an hour. Hot water is then added to a mark previously scratched on the glass to denote 205 c.c. (the 5 c.c. being necessary as a correction for the temperature), the oil being allowed to overflow. The liquid is then poured on a wet filter in order to free it from oil, and 100 c.c. of the cold filtrate titrated with $\frac{N}{2}$ NaOH using lackmoid, as indicator. Another portion of the filtrate is tested qualitatively for sulphuric and hydrochloric acid, and the number of c.c. $\frac{N}{2}$ NaOH required above worked out according to which acid is present.

Free fatty acid is estimated by weighing about 7 grms. of oil in a wide-mouthed flask. About 50 c.c. of hot neutral alcohol, together with a few drops of phenolphthaleïn, are added, and the mixture heated to boiling with constant shaking. $\frac{N}{2}$ caustic soda is then added from a burette until the liquid turns pink. The colour is best seen when the flask is placed on a white tile. This titration will give the total acid, any mineral acid present will be indicated here, together with the fatty acid, hence the number of c.c. $\frac{N}{2}$ NaOH required to neutralise the free mineral acid in the amount taken must be subtracted and the remaining number of c.c. calculated to oleic, palmitic, or stearic acid.

1 c.c. $\frac{N}{1}$ NaOH = 0·282 grm. oleic acid.

1 c.c. $\frac{N}{1}$ NaOH = 0·256 ,, palmitic acid.

1 c.c. $\frac{N}{1}$ NaOH = 0·284 ,, stearic acid.

Example.—8 grms. oil required 14·5 c.c. $\frac{N}{2}$ NaOH. This amount of oil contained mineral acid equal to 0·5 c.c. $\frac{N}{2}$ NaOH.

∴ 14·5 − 0·5 = 14·0 c.c. $\frac{N}{2}$ NaOH were necessary to neutralise the free fatty acid in 8 grms. oil.

$$\frac{14 \times 100 \times 0·282}{2 \times 8} = 24·67 \text{ per cent.}$$

free oleic acid.

Mineral and Fatty Oils (Estimation of Saponifiable Matter).—The percentage of fatty oils is determined by converting them into soap and separating the unsaponifiable substances. The latter consist of *hydrocarbons* (naturally present to a small extent in the oils, or produced during their distillation), together with *waxy bodies* extracted from wool fat by means of soap and existing in the recovered oil, or *mineral oils* added intentionally.

About 3 grms. of oil are accurately weighed in a wide-mouthed flask and boiled with 25 c.c. of 8 per cent. alcoholic potash (see below) for one hour, using a reversed condenser.

100 c.c. methylated alcohol (distilled over caustic potash) are mixed with 10 grms. solid caustic potash and allowed to stand; the clear liquid is used for these determinations.

The contents of the flask are poured through a funnel into a separator and the flask well rinsed with hot water. The liquid in the separator should have a volume of 200 c.c. When the solution is quite cold the flask is rinsed out with a few drops of alcohol and then with 50 c.c. of ether (previously distilled on a water-bath), the whole being then poured into the separator and vigorously shaken for two minutes. The cork is carefully loosened and the mixture allowed to stand for fifteen minutes. The lower layer is then run into another separator and shaken as before with 25 c.c. ether. After standing and separating, the alkaline liquid is again treated with 25 c.c. ether as above and the lower stratum is run off. The three etherial extracts are united in the first separator, the second and third vessels and the stoppers belonging to them being thoroughly washed with ether, and the washings added to the bulk of the etherial extract. Occasionally it happens that between the etherial and aqueous layers a smaller stratum of flocculent matter appears. This substance consists of insoluble soaps, and is best run off as completely as possible with the alkaline layer until three extractions have been made. The alkaline liquid is then run off, and the residual insoluble soaps which are liable to entangle unsaponifiable oil, are extracted with 25 c.c. of ether, which, after standing, is separated and added to the main quantity. The etherial extract is next shaken for two minutes with 25 c.c. of water, allowed to stand fifteen minutes and the alkaline liquid run off. The washing is repeated a second and third time in exactly the same manner. The washed etherial extract is poured into the flask originally used (clean and dry), and the separator and cork well rinsed with

ether into it. The flask is placed on a water-bath and connected with a condenser, and the ether carefully distilled off. The condenser is then removed and a few drops of alcohol added to the residual oil in order to volatilise any water present. A short heating on the water-bath suffices to remove all globules of water. The flask is then placed in a water-oven for twenty minutes, when it is taken out, cooled, and weighed. The heating should be repeated until a constant weight is obtained.

Example.—2·755 grms. oil yielded 1·255 grm. unsaponifiable oil.

$$\frac{1·255 \times 100}{2·755} = 45·55 \text{ per cent.}$$

unsaponifiable oil.

Water is estimated by heating about 10 grms. of oil in a porcelain basin with rod, with frequent stirring in a water-oven until it ceases to lose weight. Four hours is generally sufficient.

Example.—12 grms. oil lost 0·24 grm.

$$\frac{0·24 \times 100}{12} = 2·0 \text{ per cent. water.}$$

The results are stated as
Unsaponifiable oil,	.	.	45·55 p. ct.	
Water,	.	.	2·00	,,
Saponifiable matter by difference,	.	.	52·45	,,
			100·00	,,

In making the above determinations it is necessary to thoroughly agitate the sample before taking portions for analysis, and if any part of it be solid the oil should be warmed in a water-oven until quite liquid and then well mixed by shaking in a bottle.

The unsaponifiable portion of the oil may contain mineral oil. The method of detecting this is mentioned under OLEIC ACID.

The action of the oil on metals is demonstrated by leaving strips of the metals with which the oil will come in contact, immersed in the oil, either at the ordinary temperature or in the water-oven, and examining them from time to time.

Soap and other matters insoluble in ether are estimated by diluting a portion of the oil with ether, and passing it through a filter. The residue after washing with ether may be weighed and tested for soap, &c.

Mineral matters or *ash* may be determined by burning 5 to 10 grms. of the oil, and incinerating and weighing the residue.

The tendency of oils to gum is shown by allowing an equal number of drops of two samples to fall side by side on an inclined plane, and observing the distance in inches run down by the samples in a given time,

and also the length of time required before the oil ceases to run owing to its increased viscidity due to oxidation.

The flashing point is determined by heating 50 c.c. of the oil in a nickel crucible placed on a sand-bath. A Fahrenheit thermometer is suspended in the oil, the bulb being kept clear of the bottom of the crucible, and the temperature carefully observed. Meanwhile, a small gas jet from a glass tube is applied from time to time to the surface of the oil, which should be stirred continually with the thermometer. At the moment inflammable vapours are evolved, the gas jet will ignite them, and a flickering light will appear on the surface of the oil, and at the same time the faint explosion of the gas will be heard. The instant this phenomenon occurs, the height of the mercury column is accurately observed, and this temperature recorded as the flashing point.

In the case of wool oils the flashing point should not be below 340° F. (170° C.).

The congealing point is ascertained by half filling an ordinary test tube with the oil, and placing it in a mixture of salt and ice. The temperature at which it ceases to run on inclining the tube is taken as the congealing point. If the oil contains dirt or water it is necessary to filter the oil while warm through a dry filter.

LUTECIENNE (P.) a mixture of *Fast red A* and *Orange II.*

LUTEOLIN *v.* WELD.

LUTEOLIN. An obsolete acid orange.

LUTES are substances which are used for repairing cracks in vessels or for packing joints, &c.

The following lute is useful for preserving glass vessels from injury when exposed to fire:—Pipeclay and shredded tow made into a paste with water. Fractures in furnaces may be repaired by means of a paste of firebrick and liquid sodium silicate, or a mixture of powdered clay and ground bricks moistened with borax solution.

Leaks in boilers may be closed by means of a paste consisting of 6 parts of clay and 1 part of iron filings, mixed with boiled linseed oil. A lute for closing iron joints, but which requires some time to act, is prepared from 100 parts of iron filings and 2 parts of ammonium chloride mixed with a little water.

Another similar mixture, but one which sets more quickly, is obtained by mixing 100 parts of iron filings, 5 parts of ammonium chloride, or 10 parts (or, if the iron filings be fine, 20 parts) of flowers of sulphur mixed with water to a paste and applied immediately.

A waterproof cement which adheres strongly to metal, wood, or stone, and softens when heated, is made by melting 1 part of *gutta-percha* with 2 parts (by weight) of pitch until thoroughly mixed.

Among other lutes for only moderate temperatures are the following :—(1) India-rubber bands or caoutchouc dissolved in naphtha ; (2) clay and boiled linseed oil well mixed and kept in position by bladder ; (3) a mixture of equal parts of red and white lead made into a paste with linseed oil and mixed with tow will resist a fair amount of internal pressure ; (4) "soft cement," which melts easily and is readily moulded in the hand, is prepared by melting beeswax with one-eighth part of its weight of turpentine.

LUTETIENNE, old name for *Eosin.BN.*

LYDIN, old name for *Rosolan.*

M

MACLURIN *v.* Fustic.

MADDER. Before the introduction of artificial alizarin, in 1868, madder was the most important of the natural dyestuffs, with the single exception of indigo, and although now entirely replaced by the artificial product in Turkey red dyeing, it is still employed to a limited extent in wool dyeing. The enormous decrease in the amount used is, however, well shown by the following figures :—

BRITISH IMPORTS OF MADDER.

Year.					Tons.
1868,	.	.	.	.	15,292
1875,	.	.	.	.	5,014
1879,	.	.	.	.	1,073
1892,	.	.	.	.	218

The value of the fifteen thousand tons imported in 1868 was £1,052,620—*i.e.,* about £70 per ton, whereas the price is now less than £30 per ton, and even with this great reduction in cost, madder cannot compete in price with its artificial substitute.

The use of madder as a dyestuff dates from very early times. Pliny mentions it as being used by the Hindoos, Persians, and Egyptians, and madder-dyed cloth has been frequently found in the wrappings of Egyptian mummies. It was known to the Greeks under the names ερυτροδομυς and ερυθοδανον, and it is mentioned by Virgil that sandyx (madder) imparts a red colour to the bones of pigs which have fed upon it. This observation has been frequently corroborated, the development of the red colour being due to the formation of calcium alizarate from the phosphate of lime in the bones. In the middle ages, the names *sandis, warantia, granza, garancia,* were applied to madder, the latter being still retained in France (garance).

The madder plant is indigenous to India and Central Africa, and in Europe was probably first cultivated in Spain, being introduced from Algeria by the Moors. It was grown in Holland as early as the tenth century, and first introduced into Italy and France about the time of the Crusades, records showing that it was cultivated in Marseilles in 1287. It was not, however, grown in Avignon until 1666, and is first noted in Alsace in 1729. The cultivation of madder has frequently been attempted in England. As early as 1624, and again in 1670, licences were issued to certain individuals, granting the privilege of growing madder on payment of a tax equal to the import duty on foreign madder. At a later period the Society of Arts made great efforts to acclimatise the industry, granting for home-grown madder upwards of £1500 in premiums, in addition to many medals, during the latter half of the eighteenth century. The cultivation of madder in England has, however, never been commercially successful, although there is no difficulty in growing the plant on a small scale.

Origin.—The plants which produce madder are several species of *Rubia,* a genus of Galiaceæ (natural order, *Rubiaceæ*). They are herbaceous perennials, having a quadrangular stem, with whorls of lanceolate leaves. They bear a small yellow flower, which fructifies in the form of a dark red berry. The various species appear to thrive best under somewhat different conditions, but generally a moist, loose, rich soil gives the best result. The colour-yielding substance resides almost entirely in the roots, which alone are valuable ; they attain a length of from 1 to 3 feet, and in thickness vary from a quarter to half an inch.

The following are the chief species of madder plants :—

Rubia tinctoria.—This is grown in Western Europe, especially France and Holland, and to a small extent in the United States.

Rubia peregrina is cultivated chiefly in the Levant and in Provence, and is occasionally found in the wild state in England. This variety is said to produce somewhat brighter shades than *Rubia tinctoria.*

Rubia munjista is the chief madder plant of India, East Indies, Japan, and China. The root is known as *munjeet,* and is very rich in colouring matter.

Rubia cordifolia is also grown in China and Japan. *Oldenlandia umbellata* (syn. *Hedyotis umbellata,* is the source of the *Che* or *Chay* root used in Coromandel and other parts of India.

Morinda citrifolia, which yields the *Al* or *Sooranjee* of the Hindoos, is used locally in Oudh and Madras.

Galium tinctorium and several other species of *Galium,* as well as *Asperula tinctoria* (dyers' woodruff) are also employed in the localities in which they are found. The former are native to the United States and Canada, the latter to Great Britain.

Cultivation and Preparation of Madder.

In the cultivation of madder the plants are allowed to mature for three years (in France and Holland), or for five years (in Eastern Europe). The roots are then removed from the ground, cleaned from adhering earth, and dried either in the air or by artificial heat. A broken or cut surface of the dry root exhibits a reddish-yellow colour, which quickly becomes deep red if moistened.

Turkish madder is usually sold in the form of the dry root, but most other varieties are more or less finely ground. During the grinding three qualities may be separated :—

(1) The skin or bark of the root, which separates with slight pressure, and which contains little colouring matter. This is termed "mull" madder.

(2) The annular portion of the root in which the colouring matter principally resides.

(3) The central ligneous portion, which, like the bark, contains little colour.

Frequently the second and third portions are mixed. Ground madder is also distinguished as "cropped" and "uncropped." "Crop" madder has the outer bark ("mull") removed before grinding, and is therefore correspondingly richer in colouring matter ; whereas when "uncropped" the whole root is ground together. After grinding, the madder is packed into casks, and usually stored for a varying length of time, during which a change — which will be explained later—takes place, resulting in a great increase in colouring power. During storage in the cask the madder becomes darker in colour, swells up, cakes together, and sometimes bursts the casks. If stored for too long a time, it becomes brown and worthless.

Commercial Varieties. — Commercially, the different varieties of madder are distinguished by the names of the localities from which they originate, the following being the chief kinds with their principal characteristics :—

(1) *Dutch madder* comes into the market in a coarsely ground condition. It has a strong, unpleasant smell, and varies in colour from orange-red to brown, the latter being inferior. It is very hygroscopic, the colour changing to rich dark red as moisture is absorbed. Dutch madder is grown in sandy soil, and contains a considerable amount of pectic matters. It is always stored for at least one year, and is in its prime after three years' storage. It may, however, be kept for five or six years, but after that time gradually deteriorates.

(2) *Alsatian madder* is generally similar to Dutch, but of inferior quality. It is usually stored for about two years, and deteriorates more quickly than Dutch madder.

(3) *Avignon Madder.*—This varies greatly according to the nature of the soil upon which it is grown. The two principal varieties are :—*Palus* (P.) which grows on marshy ground, and *Rosæ* (R.) produced by chalky soil. The first mentioned is most esteemed. Avignon madder has a pleasant smell, and is dry and easily powdered. It is much richer in colour than Dutch or Alsatian, contains less pectic matters and is less hygroscopic. The fermentation during storage is, therefore, much less marked, and, indeed, it is frequently used when freshly ground, though improved by storage for a year.

(4) *Levant* or *Turkish madder* is sold in the unground condition. It is exported from Smyrna, Cyprus, &c., and is of good quality.

(5) *Italian* or *Naples madder* is also of good quality, and is sold in the root. The different varieties of madder yield somewhat different shades, according to the proportion of colouring matters (alizarin and purpurin) present, and the amount of chalk, pectic matters, &c., which they contain.

Chemistry of Madder.

When freshly dug up, madder root contains about 80 per cent. of moisture, but after drying for sale this is reduced to about 15 to 20 per cent. In this, as in other respects, however, different samples vary greatly, although all contain a large proportion of extractive substances, consisting mainly of sugary and gummy matters, starch, pectic acid, &c.

Considerable practical interest attaches to the extractive matters above referred to, not only when madder is used as a dyestuff, but also when it is employed as a means of generating fermentation in the indigo vat ; indeed, in the latter case the value of the madder is almost entirely due to these bodies. In the dyeing of Turkey-red upon cotton, the brown and yellow impurities are so completely removed by the subsequent clearing processes that a most brilliant colour is obtained, but it is practically impossible to produce the same bright colour upon wool on account of the permanent fixation of the impurities.

The elucidation of the chemical changes which occur in madder root during storage, &c., is principally due to the classical researches of Schunck. The growing or freshly-cut root contains no ready formed colouring matter. In this respect, madder is similar to many other of the natural dyestuffs, these usually containing, while growing or when freshly gathered, certain *colouring principles*, which are in themselves quite devoid of colour or of dyeing power. By subsequent oxidation or decomposition the *colouring principles* are, however, converted into the *colouring matters* upon which the dyeing depends.

In madder, the colouring principle is a glucoside, *rubian*, which, by the action of a peculiar ferment, *erythrosym*, is decomposed, yielding several products, the chief of which is the colouring matter, *alizarin*. It seems clear that the principal change which takes place during the storage of madder is this decomposition of rubian, with slow production of alizarin, but it is uncertain whether the simultaneous formation of purpurin is due to oxidation of a portion of the alizarin during some stage of the process, or is a product of the decomposition of a distinct glucoside.

Rubian has the composition $C_{28}H_{30}O_{15}$. It was first isolated by Schunck, who prepared it in the following manner:—Fresh madder root is extracted with boiling distilled water, and the filtered solution treated with animal charcoal, which absorbs the rubian and chlorogenin. The charcoal is then collected on a filter, and washed with cold water to dissolve the chlorogenin, after which the rubian is dissolved by treating the charcoal with successive portions of alcohol, and is obtained by evaporation of the solvent. When thus prepared it forms a dry, brittle, amorphous mass of a gummy nature. It is soluble in hot water or alcohol, but insoluble in ether, and is not precipitated from solution by metallic salts.

Rubian is readily decomposed by acids and alkalies, as well as by the special ferment, *erythrosym*, which has been already mentioned, but the products obtained are not identical, as will be seen by the following table :—

Decomposition of Rubian.

By Fermentation.	By Mineral Acids.	By Alkalies.
Glucose.	Glucose.	Glucose.
Rubiafin.	Rubianin.	Rubiadin.
Rubiretin.	Rubiretin.	Rubiretin.
Verantin.	Verantin.	Verantin.
Alizarin.	Alizarin.	Alizarin.

Ruberythric acid, first obtained by Rochleder, is a simple glucoside of alizarin, and, unlike rubian, decomposes without the formation of by - products. Schunck, who proposes the name *rubianic acid* for this body, maintains that it does not exist in madder root, but is an oxidation product of rubian.

Erythrosym appears to contain lime as an essential constituent, its formula being $C_{56}H_{34}N_2O_{40} + CaO$ (Schunck). If the lime is removed by treatment with an acid, the erythrosym loses its power of inducing fermentation.

Erythrosym may be prepared by extracting madder root with water at a temperature of 30° C. and precipitating the filtered solution with alcohol. When dried it forms a brown, amorphous mass, and has the power of rapidly decomposing a solution of rubian. It does not, however, decompose other glucosides.

Erythrosym is soluble in cold water, from which solution it is precipitated by alcohol. On boiling its aqueous solution it is coagulated and precipitated, and loses its power of inducing the decomposition of rubian; and this explains the well-known fact that fuller and richer colours are obtained when the madder dye - bath is maintained at a low temperature for a considerable time, so that the erythrosym may have sufficient time to decompose the rubian, which is always present even in madder which has been stored for a long time.

Madder Colouring Matters.

Madder contains two colouring matters, *alizarin* and *purpurin*, but the latter is usually present in insignificant amount. The total amount of the two in commercial madders varies from 1·5 to 2 per cent.

Alizarin, $C_{14}H_8O_4$, is the principal colouring matter of the madder root, from which it was first obtained in 1824 by Robiquet and Colin. It may be obtained by extracting ground madder root with a solution of sulphurous acid, to which a little hydrochloric acid is added. The glucoside solution thus produced is heated with sulphuric acid, when red-coloured flakes of crude purpurin separate out, the clear liquid, after being boiled and cooled, depositing crude alizarin as a greenish powder. To obtain a pure product this is extracted with hot petroleum, the solution filtered and evaporated to crystallisation.

Alizarin is now manufactured on an enormous scale from *anthracene*, one of the coaltar hydrocarbons. When pure, alizarin forms large, needle-shaped orange-red anhydrous crystals. It melts at 290° C., is insoluble in cold water, but dissolves to a slight extent in boiling water (0·34 grm. per litre), forming a pale yellow solution. It is readily soluble in alcohol, ether, glycerol, benzene, carbon disulphide, and turpentine. It may be obtained in crystals containing 2 or 3 molecules of water, the dihydrate being produced by crystallising from aqueous alcohol, and the trihydrate from moist ether. It dissolves in concentrated sulphuric acid, and is precipitated unchanged on dilution with water.

Alizarin is a very stable body, but yields many interesting and valuable derivatives by the action of powerful reagents. When

15

distilled with zinc, *anthracene* is obtained ; this reaction leading Graebe and Liebermann to a correct view of the composition of alizarin, and ultimately to its artificial preparation. Mild oxidising agents have no action on alizarin, but by the action of powerful reagents, such as anhydrous sulphuric acid, with or without addition of manganese dioxide, oxidation takes place with production of a series of new dyestuffs.

Many other colouring matters are also obtained from alizarin, which may be considered the basis of an extensive and important series of dyes.

By reason of the hydroxyl (OH) groups which it contains, alizarin readily forms lakes with metallic oxides. The alkalies form readily soluble salts which possess an intense purple colour ; but the heavy metals produce insoluble compounds, the colour of which varies according to the metal employed (*v.* ALIZARIN).

Purpurin ($C_{14} H_8 O_5$). — This colouring matter exists in madder, but is present in much smaller amount than alizarin. It closely resembles that body in appearance and properties, but may be distinguished by the colour of its alkaline solution, which is cherry-red instead of purple. The alkaline solution of purpurin is also slowly decolorised by exposure to air, whereas the colour of the alkaline alizarin solution is permanent. The absorption spectra of alizarin and purpurin in alcoholic solution are quite distinct.

Purpurin is artificially obtained by oxidising alizarin with manganese dioxide and sulphuric acid at a high temperature, and may also be prepared in other ways. In dyeing it gives somewhat bluer shades than alizarin.

Rubiretin and Verantin are resinous bodies which always accompany alizarin in its production from rubian, by whatever means the glucoside is decomposed. They are not colouring matters.

Xanthin.—As early as 1825-30 Kuhlmann obtained a yellow substance from madder, which was long supposed to be an injurious impurity, giving a brown tinge to the Turkey red. Schunck has since shown, however, that this body (xanthin) is a combination of rubian and chlorogenin.

Chlorogenin, also called *rubichloric* acid, is a dark green amorphous substance found partially in the free state and partially in combination with rubian.

MADDER PREPARATIONS.

Although the various commercial preparations of madder are now very little, if at all, employed, and were never much used in wool dyeing, it is perhaps desirable to refer to them in a brief manner.

Garancin was formerly much used by the calico printer. It is prepared in the following manner :—100 lbs of ground madder are mixed with 100 gallons of cold water, and allowed to steep for twelve hours ; 35 lbs. of strong sulphuric acid are then added, and the mixture boiled by means of steam for four to five hours. After adding a large quantity of cold water, the mixture is drained, washed free from acid, dried and ground. These quantities yield from 30 to 40 lbs. of garancin, which, however, is equal in dyeing power to 120 to 150 lbs. of the original madder, the increase in tinctorial effect being due to the fact that never more than two-thirds of the absolute dyeing power of madder is rendered available in an ordinary dyeing process.

The production of garancin is based upon the observation that alizarin is unaffected by treatment with sulphuric acid, while much of the woody and extractive matter present in the madder root is destroyed or rendered soluble thereby. Any rubian present is, of course, decomposed with production of alizarin.

Garanceux is garancin made from spent madder—that is, madder which has been employed in dyeing. Its production, therefore, constitutes a method of utilising the whole of the colouring matter.

Commercial alizarin or Pincoffin was first prepared by Schunck and Pincoffs, who found that when garancin is submitted to high-pressure steam (at 150° C.) for about twelve hours almost the whole of the impurities are destroyed. The product has at least twenty times the dyeing power of ground madder.

Madder extracts may be prepared in several ways ; for instance, garancin may be extracted with boiling water containing a trace of sulphuric acid, and the solution filtered, when on cooling an orange coloured precipitate of impure alizarin separates out, which has about fifty times the colouring power of madder.

Madder lake, which is much used as a red pigment in oil painting, is now prepared from artificial alizarin, but the following method, in which madder is used as a basis, will be of interest :—Ground madder is well washed with a cold solution of sodium sulphate, and is then boiled with a 10 per cent. solution of alum. This produces a red solution, which is filtered and allowed to cool to 35° C. Seventy-eight parts of lead acetate for each 100 parts of alum is then added, and after filtering off the deposited sulphate of lead the solution is boiled, whereupon a brilliantly coloured alumina lake of alizarin separates out.

VALUATION OF MADDER.

The simplest and most reliable method of estimating the comparative value of different

samples of madder in wool dyeing is by means of a small dyeing trial. The experiment should be made upon wool previously mordanted, either with bichromate of potash, or alum and tartar, choice being made of that mordant which will on the larger scale be principally employed.

If equal weights of the samples are used in dyeing, the one richest in colouring matter is readily detected, but if the prices of the different samples are known the equal weights may conveniently be replaced by quantities which represent equal *costs*, a standard amount of the highest priced, and a proportionally larger amount of the lower priced samples, being taken.

When comparing different varieties of madder, such, for instance, as Avignon with Dutch, it is necessary, particularly when alum is the mordant used, to take account of the fact that the amount of chalk which they naturally contain differs considerably. Preliminary experiments should, therefore, be made, adding to each sample various amounts of chalk, the comparison of the samples being then made, using with each that amount of chalk which was found to give the best result.

Since the amount of undecomposed rubian in the samples may also vary, it is necessary to raise the temperature of the dye-bath very slowly in order to prevent loss of colouring matter, which might otherwise occur, as explained above, by destruction of the ferment.

APPLICATION OF MADDER.

When thoroughly cleansed wool is boiled in distilled water with pure alizarin, it acquires a reddish-brown colour of considerable intensity and permanence. This colour is quite distinct from that of the alizarin itself, and is probably due to a chemical combination between the wool fibre and the dyestuff. If the water contains even a trace of lime salts a much redder shade is obtained, the calcium probably acting as a mordant, with production of calcium alizarate upon the fibre.

The colour obtained by boiling unmordanted wool with madder varies from pale salmon-red to dark brownish-red, according to the amount used, this method of dyeing being actually employed for the production of pale salmon-pinks and drabs. At first sight this process appears somewhat irrational, since madder requires to be used in conjunction with a mordant for proper fixation and development of the colour; but further consideration shows that the colour produced is really due for the most part to the fixation of calcium or magnesium alizarin lakes, though the true colour of these is, of course, considerably modified by the yellow and brown extractive matters present.

It has already been incidentally mentioned that madder is employed as a means of promoting fermentation in the indigo (woad) vat. Although it is not in this case used as a dyestuff, there is always a notable amount of colouring matter fixed, probably as a lime lake, as may be often recognised when testing indigo dyed cloth.

Before the introduction of artificial alizarin, madder was very largely used by the wool dyer, both for producing red shades and as the red or brown constituent of compound shades—*i.e.*, browns, olives, greys, &c. ; and although artificial dyes, particularly nitro-alizarin and anthracene brown, have largely replaced madder for these purposes, it is still used in dyeing closely felted material—such, for instance, as felt hat bodies—on account of its penetrative power, in which respect it is much superior to its artificial substitutes.

With the different mordants madder gives a considerable variety of shade, as will be seen by reference to the following table :—

| Mordant.	Colour Obtained.
Chromium.	Reddish-drab to claret-brown.
Aluminium.	Pink to dull scarlet.
Iron.	Drab to purplish-brown.
Copper.	Drab to yellowish-brown.
Tin.	Brownish-orange.
Zinc.	Reddish-brown.
Uranium.	Purplish-brown.
Manganese. Nickel. Cobalt.	} Reddish-brown.

MADRAS BLUE. This name has been applied to a mixture of *Gallocyanine* and *Logwood extract*.

MAGDALA RED (D. & H.). *Naphthylamine red* (D. & H.), *Fast pink for silk* (D. & H.), *Naphthaline red, Sudan red.* An azine dye. *Diamido-naphthyl rosinduline chloride.* 1868. Dark brown powder, slightly soluble in boiling water. In concentrated H_2SO_4, greyish-violet solution ; on dilution, violet-red ppt.

Application.—A basic colour. Dyes *silk* red with fluorescence from a soap bath.

MAGENTA (All makers). Pure qualities are known as *Fuchsine, Rubine, Aniline red, Roseine ;* crude qualities are sold under the names *Maroon, Grenaldine, Geranium, Cerise, Russian red, Azaleine, Solferino, Erythrobenzin, Rubianin, Harmalin.* Commercial magenta (pure) consists of the

acetate, hydrochloride or (less commonly) *sulphate of para-rosaniline* and *rosaniline*.

Para rosaniline salt.　　　Rosaniline salt.
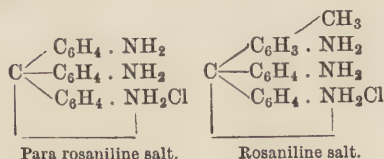
(For further information see ROSANILINE). 1858. Impure magentas contain *phosphine*, &c. The *hydrochloride* forms green glistening crystals, the *acetate* is usually sold as glistening lumps, and the *sulphate* as a fine green crystalline powder. All are soluble in water or (more easily) in a mixture of alcohol and water. In concentrated H_2SO_4, yellowish-brown solution, which is almost decolorised on dilution. Magenta solutions are decolorised by reducing agents or by alkalies, the colour being restored by oxidation or by acids respectively.

Application.—A basic dye. Dyes *wool*, *silk*, *leather*, or tannin - mordanted *cotton* bluish-red from a neutral bath. Used largely in the manufacture of the rosaniline blues and violets. (See also NEW MAGENTA.)

MAGENTA BASE *v.* ROSANILINE.

MAGNESIA ALBA *v.* MAGNESIUM CARBONATE.

MAGNESITE *v.* MAGNESIUM.

MAGNESIUM, Mg = 24. The principal compounds of magnesium which occur in nature are *magnesite* ($MgCO_3$), *kieserite* ($MgSO_4 . H_2O$), *dolomite* ($MgCO_3,CaCO_3$), *talc*, and other *silicates*.

Preparation.—The metal may be prepared by heating a mixture of magnesium chloride and sodium chloride with sodium. Calcium fluoride is also added as a flux.

$$MgCl_2 + 2Na = 2NaCl + Mg.$$

On extracting the mass with water the metal remains undisturbed. The crude magnesium is purified by distillation in absence of air.

Properties.—Magnesium is a white metal similar to silver. Moist air, however, causes it to tarnish owing to the formation of a film of the oxide. When warmed it can be rolled and pressed. On heating, it takes fire and burns with a brilliant white light. It is used in signalling, in pyrotechny, in photography, and for matching colours when daylight is not available.

Dilute acids dissolve the metal with formation of salts ; alkalies have no action on it.

Magnesium acetate, $Mg(C_2H_3O_2)_2$, is prepared by dissolving magnesium carbonate in acetic acid, or by treating lead acetate with magnesium sulphate. It is readily soluble in water, from which it crystallises with 4

molecules of water. H. Koechlin has proposed it as a mordant. It plays the part of an alkali in printing colours on calico.

On treating the normal acetate with magnesia, a basic acetate having antiseptic and deodorising properties is produced.

Magnesium Carbonate, $MgCO_3$. — The carbonate of magnesium occurs as *magnesite* and *dolomite*.

Magnesia alba is a commercial basic magnesium carbonate. It is formed when sodium carbonate is added to a solution of magnesium sulphate or chloride. The white precipitate when dried forms a voluminous powder.

Magnesium carbonate is almost insoluble in water. The aqueous solution turns reddened litmus blue. Solutions of carbon dioxide dissolve the carbonate.

Magnesium Chloride, $MgCl_2$.—This salt is present in sea water and in many springs.

Preparation.—It may be obtained by dissolving magnesium oxide or carbonate in hydrochloric acid. On the large scale it is formed as a by-product in the manufacture of potassium chloride from *carnallite* ($KCl . MgCl_2 . 6H_2O$). After concentrating the mother liquors from the potassium chloride manufacture in order to separate sodium and potassium chlorides and sulphate of magnesia, the hot concentrated solution is run directly into casks in which it solidifies. It thus forms a white mass containing half its weight of $MgCl_2$.

Properties.—Magnesium chloride is very deliquescent and easily soluble in water. On being heated it decomposes, forming *magnesium oxychloride*, $MgCl(OH)$, and hydrochloric acid. Water containing much magnesium chloride is not suitable for use in steam boilers, because the acid which is set free corrodes the iron. Magnesium chloride is employed by cotton spinners as a thread lubricator, and as an ingredient of sizes. It is used in the "carbonisation" of cotton in woollen goods, its action depending on the fact that the salt when applied to the vegetable fibre is decomposed into magnesia and hydrochloric acid by the water which is present in the fibre.

F. Breinl and C. Hanowsky* have arrived at the following conclusions with regard to the practical application of this salt in the process of carbonisation :—

1. A magnesium chloride solution of 13° Tw. is sufficient in all cases, as even cotton (of all vegetable fibres the most difficult to destroy) is thereby completely destroyed ; not only becoming tendered but turning black.

2. Materials saturated with magnesium chloride must be well dried at a low temperature in order to prevent a large evolution of steam in the carbonising chamber and its consequent condensation, and the drying

* *Journ. Soc. Dyers and Col.*, 1892, p. 208

chambers must be well ventilated, as otherwise there is, on the one hand, danger of the material becoming spotted with the drops of condensed steam, and, on the other hand, in consequence of the property that magnesium chloride possesses of becoming easily decomposed in the presence of steam, there is a possibility that the colour produced on dyeing may be seriously affected by the magnesia which separates out on the fibre.

3. A temperature of 140° to 150° C. in the carbonising chamber will suffice to destroy all vegetable fibres mixed with the wool. Above 150° C. the wool fibre is affected.

4. In carbonising wool rich in burrs, which has been dyed with colours sensitive to the action of alkalies, the magnesia will have a detrimental effect. On the other hand, a treatment with dilute acid after the carbonising will be injurious to wool dyed with colours which are sensitive to the action of acids.

Magnesium hydrate, $Mg(OH)_2$, is precipitated as a white powder when sodium carbonate is added to a solution of a magnesium salt. It occurs native as the mineral *brucite*. It is insoluble in water, but dissolves in dilute acids. Fatty acids combine with it to form insoluble soaps. Moist magnesium hydrate has an alkaline reaction. On gently heating the hydroxide, magnesia (MgO) is formed. Magnesium hydrate absorbs carbon dioxide from the air, being converted into magnesium carbonate.

Magnesium Oxide, MgO. — *Magnesia* is produced by burning the metal, or by igniting the carbonate or nitrate in the air. It is known as *calcined magnesia* and is used in medicine. It is only fusible at a high temperature, and is employed in the manufacture of fire-bricks, crucibles, &c.

Magnesium sulphate ($MgSO_4$) occurs in nature as *kieserite* ($MgSO_4 + H_2O$), and as *Epsom salts* ($MgSO_4 + 7H_2O$). The former is almost insoluble in water, the latter is soluble in three parts at 15° C. It is prepared on the large scale from kieserite and magnesite, and occurs in commerce in rhombic crystals or as a crystalline powder. Magnesium sulphate is used in medicine, in wool dyeing (for some basic colours), and in the finishing of cotton goods. If used for the latter purpose, it should not contain any magnesium chloride, as the latter is liable to generate hydrochloric acid in the free state at the temperature of the calender roller, and thus might tender the fibre. Magnesium sulphate is the only magnesium compound which is largely used in dyeing.

MAISE *v.* CURCUMIN S.

MALACHITE *v.* COPPER.

MALACHITE GREEN (all makers). *Benzal green* (O.), *Benzoyl green*, *New Victoria green* (B.), *New green* (By.), *Solid green cryst*

(C.), *Solid green O* (S.C.I.), *Diamond green* (Mo.), *Diamond green B* (B.), *Dragon green*, *Bitter almond oil green. Zinc chloride double salt, oxalate, sulphate, or picrate of tetramethyl diamido triphenyl carbinol.* 1877. The *zinc chloride double salt* forms brass-yellow prismatic crystals; the *oxalate* metallic green glistening plates, giving a bluish-green solution in water. In concentrated H_2SO_4, yellow solution, which becomes green on dilution with water.

Application.—A basic colour. Dyes *wool, silk, leather, jute,* or tannin-mordanted *cotton,* bluish-green from a neutral bath.

MALACHITE GREEN G (B.) *v.* BRILLIANT GREEN.

MALTA GREY (P.) *v.* METHYLENE GREY (M.).

MANCHESTER BROWN *v.* BISMARCK BROWN.

MANCHESTER BROWN EE (C.) (Lev.). *Manchester brown P S* (C.). *A Bismarck brown from meta-toluylene diamine.*

MANCHESTER YELLOW (Lev.) *v.* MARTIUS YELLOW.

MANDARIN G EXTRA (Ber.) *v.* ORANGE II.

MANDARIN G R (Ber.) *v.* ORANGE T (K.).

MANGANESE, Mn = 55. The chief ores of manganese are *pyrolusite*, MnO_2; *braunite*, Mn_2O_3; *hausmannite*, Mn_3O_4; *manganite*, $Mn_2O_3 . H_2O$; *diallogite*, $MnCO_3$; and *manganese blende*, MnS.

Manganese is prepared by heating manganese carbonate with carbon, the oxide formed being reduced to metallic manganese. The metal is very hard and is melted with difficulty. It is employed as an alloy with iron and in some bronzes.

Manganous chloride, $MnCl_2$, is obtained on the large scale as a by-product in the manufacture of chlorine by treating manganese dioxide with hydrochloric acid (see below). The acid solution of crude manganous chloride is evaporated to free it from acid, then treated with one-quarter the amount of sodium carbonate required to precipitate the manganese and iron, boiled, and filtered from ferric hydrate. Cobalt and nickel are removed by the addition of manganese sulphide. Copper, if present, should be precipitated with hydrogen sulphide. On addition of sulphide of ammonium the manganese is thrown down as sulphide. After washing, it is dissolved in hydrochloric acid, concentrated and crystallised.

It forms monoclinic pink-coloured deliquescent crystals, which contain 4 molecules of water of crystallisation. It is soluble in water and in alcohol; the alcoholic solution when ignited burns with a red flame. 100 parts of water at 10° C. dissolve 150 parts;

at 31°, 269 parts; and at 62·5° C., 625 parts of the salt $MnCl_2 + 4H_2O$.

Manganese chloride is used in dyeing cotton manganese-brown or bronze. The cotton is impregnated with a solution of the salt, passed through caustic alkali, and the precipitated hydroxide is oxidised by the air or other oxidising agents to form brown manganic hydroxide. The oxidising power of manganic hydroxide which has been thus deposited in the fibre may be used for the production of aniline black. The liquor comes into commerce as a reddish solution at about 70° Tw. It often contains a considerable amount of calcium chloride, which renders it comparatively useless for dyeing operations. It ought not to contain more than 1 per cent. calcium chloride.

Analysis.—Manganous chloride is tested by steeping similar weights of cotton in a solution of the sample to be tested and in a standard sample, both at 30° C. After squeezing out and drying they should be dipped for six seconds in a boiling solution of caustic soda at 30° Tw., washed, and finally oxidised in a very weak bleach solution for twenty minutes. Or, a known weight of the manganous chloride is diluted, and the manganese precipitated as hydrated peroxide, with bromine in a slightly ammoniacal solution. The beaker containing the precipitate is left in a warm place with the addition of a little more ammonia, and the solution eventually filtered after adding a few drops of alcohol. After washing, the precipitate may be re-dissolved in hydrochloric acid, reprecipitated as before, and after drying and igniting, weighed as Mn_3O_4.

Manganous hydroxide, $Mn(OH)_2$, is precipitated from the solutions of manganous salts as a white gelatinous mass that rapidly turns brown by absorption of oxygen. It is soluble in most acids and is a diacid base; the salts are colourless or pink, and do not absorb oxygen. Manganous hydroxide is insoluble in caustic alkalies. Sulphide of ammonium precipitates manganous sulphide from the solutions of manganous salts; sulphuretted hydrogen has little action except in the presence of free alkali.
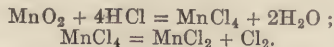
MANGANESE OXIDES.

Manganese monoxide, MnO, is formed by heating manganese carbonate or any oxide of the metal in hydrogen. It is a green powder which quickly oxidises, forming red oxide (Mn_3O_4).

Manganic oxide, Mn_2O_3, is formed as a black powder when any one of the other oxides is heated in oxygen gas.

Manganic hydroxide, $Mn_2(OH)_6$, is a dark brown precipitate obtained by the oxidation of manganous hydroxide. It is a weak hexacid base, insoluble in alkalies and not readily soluble in acids. It does not form well-defined salts.

Manganese dioxide, MnO_2, peroxide of manganese, the common black ore of manganese or *pyrolusite*, is an almost black crystalline mass. Manganese dioxide forms hydroxides which act as very weak bases and acids. The salts which it forms with acids are called manganic salts; those in which it combines with bases are the manganites. Manganese dioxide dissolves in cold hydrochloric acid without evolution of chlorine; but on heating the $MnCl_4$ dissociates into manganous chloride and chlorine:—

$$MnO_2 + 4HCl = MnCl_4 + 2H_2O ;$$
$$MnCl_4 = MnCl_2 + Cl_2.$$

The use of manganese dioxide in the manufacture of chlorine gas, chloride of lime, and chlorates, is based on this reaction.

Potassium manganate, K_2MnO_4, is obtained as a bright green mass, when an oxide of manganese is fused in the air with caustic potash. The aqueous solution yields this salt in a crystalline form; on standing, however, or when acidified, the green colour of the solution is changed into bright purple, and a new salt *potassium permanganate*, $KMnO_4$, is formed (see below), whilst hydrated manganese dioxide is deposited:—

$$3K_2MnO_4 + 4HCl$$
$$= 2KMnO_4 + Mn(OH)_4 + 4KCl.$$
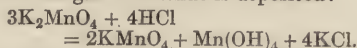
Inversely, potassium permanganate is reduced to potassium manganate by boiling it with a concentrated solution of caustic soda, and by the action of reducing agents. *Manganic acid*, H_2MnO_4, is unknown in the free state.

Manganese heptoxide, Mn_2O_7, and the hydrate, *permanganic acid*, $HMnO_4$, are unstable and little known compounds.

Potassium Permanganate, $KMnO_4$. *Permanganate of potash.* This substance is found in commerce in the form of almost black crystals with a purple-green lustre. It dissolves with an intense violet colour in 16 parts of cold water.

Potassium permanganate is prepared by heating a mixture of manganese dioxide, potassium chlorate, and caustic potash, and extracting the partly fused mass with water.

Permanganate of potash is a very powerful oxidising agent in acid, in alkaline, and in neutral solutions. Hence, it is largely used in the laboratory, and as a disinfectant (Condy's fluid), and it is sometimes employed to destroy colours on the fibres which cannot be removed in any other way. Some dyers use it to produce manganese bronze, and it has been suggested as a substitute for chlorine in the preparing of wool for printing.

Solutions of the salt cannot be filtered through paper as it is rapidly attacked.

MARBLE *v.* CALCIUM CARBONATE.

MARIGOLD (*Tagetes patula*) gives a brilliant and pure yellow with alum mordant.

MAINE BLUE B (S.C.I.) *v.* METHYL BLUE FOR SILK.

MAROON. An impure *magenta*.

MAROON S. An impure *acid magenta*.

MARS RED G (B.). An acid red.

MARTIUS YELLOW. *Naphthol yellow, Naphthylamine yellow* (R.), *Gold yellow* (D. & H.), *Primrose, Manchester yellow* (Lev.), *Naphthalin yellow* (C.) (D.) (F.). A nitro compound. *Ammonium, sodium, or calcium salt of dinitro alpha-naphthol.* 1864. *Ammonium* or *sodium* salt, forms orange-red glistening plates; *calcium* salt, yellowish-red crystals. All are soluble in water or alcohol with a yellow colour. The sodium salt deflagrates, the ammonium salt burns quietly on heating. Soluble in concentrated H_2SO_4 with greenish-yellow solution, which becomes yellow on dilution.

Application.—An acid colour. Dyes *wool* and *silk* golden yellow from an acid bath. Used also in colouring spirit lakes.

MASSICOT *v.* LEAD (OXIDES).

MAUVE, MAUVEIN *v.* ROSOLAN OR PERKIN'S VIOLET.

MEKONG YELLOW G (D. & H.). An azo dye.

$$\text{Benzidine} < \begin{matrix} \text{Salicylic acid.} \\ \text{Dioxydiphenylmethane.} \end{matrix}$$
$$\text{Benzidine} < \begin{matrix} \\ \text{Salicylic acid.} \end{matrix}$$

1893. Yellowish-brown powder, soluble in water. In concentrated H_2SO_4, violet solution; on dilution, brown ppt.

Application.—A direct cotton colour. Dyes *cotton* greenish-yellow from a soap bath.

MEKONG YELLOW R (D. & H.). An azo dye.

$$\text{Tolidine} < \begin{matrix} \text{Salicylic acid.} \\ \text{Dioxydiphenylmethane.} \end{matrix}$$
$$\text{Tolidine} < \begin{matrix} \\ \text{Salicylic acid.} \end{matrix}$$

1893. Dark brown powder soluble in water. In concentrated H_2SO_4, blue-violet solution; on dilution, black-brown ppt.
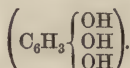
Application. — A direct cotton colour. Dyes *cotton* yellow from a soap bath.

MELDOLA'S BLUE *v.* NEW BLUE R (C.).

MELTING POINT OF FATS *v.* SOAP ANALYSIS.

MERCERISATION *v.* COTTON (CELLULOSE).

METAGALLIC ACID (*v.* also GALLIC ACID).

$$\left(C_6H_3 \begin{cases} \text{OH} \\ \text{OH} \\ \text{OH} \end{cases} \right).$$

Is isomeric with *pyrogallol* and *phloroglucinol.* It is produced by the dry distillation of tannic or gallic acid at a high temperature.

METAMINE BLUE B and G (L.) *v.* NEW BLUE B (C.).

METANIL ORANGE I and II (L.). Azo colours obtained from *meta-diazobenzene sulphonic acid* and *alpha-* and *beta-naphthol* respectively. They are acid dyes.

METANIL YELLOW (Ber.) (O.) (B.) (D.) (D. & H.) (G.) (K.). *Orange M N* (L.), *Tropaeoline* (C.), *Victoria yellow O* (M.), *Yellow G A.* An azo dye.

Metasulphanilic acid — Diphenylamine.

1879. Brownish-yellow powder, soluble in water. In concentrated H_2SO_4, violet solution, which becomes magenta-red on dilution.

Application.—An acid dye. Dyes *wool* or *silk* orange-yellow from an acid bath.

METAPHENYLENE BLUE B (C.). An azine derivative. *Dimethyltolyl tolylsafranine chloride.* 1888. Black powder, soluble in water, with a violet-blue colour. In concentrated H_2SO_4, bluish-grey solution, which, on dilution, becomes dark blue.

Application.—A basic dye. Dyes tannin-mordanted *cotton* indigo blue.

METAVANADATE OF AMMONIUM *v.* AMMONIUM VANADATE.

METHYL ALCOHOL, CH_3OH. *Wood spirit.* Is one of the products of the destructive distillation of wood.

Preparation. — The distillate from the above-mentioned process is separated from tarry matters by filtration, and treated with lime to neutralise the acetic acid, the mixture being then distilled in sheet iron boilers by direct fire heat. The distillate is re-distilled with lime from a copper still heated by a steam coil, and eventually treated with a little sulphuric acid (to neutralise ammonia), and again distilled.

Properties.—Methyl alcohol is a colourless liquid with a spirituous odour. The crude spirit has a specific gravity of about 0·85. It boils at 66° C., and burns with a pale blue flame. It is miscible with water, alcohol, and ether. Mixtures of methyl alcohol and water possess nearly the same specific gravities as those of ethyl alcohol and water. Methyl alcohol strongly resembles ethyl alcohol in its general properties.

Commercial wood spirit varies considerably in composition; the methyl alcohol ranges from 35 to 95 per cent. The impurities are aldehyde, allyl-alcohol, acetone, and other ketones, and occasionally empyreumatic bodies.

According to M. Kramer,* wood spirit used in the manufacture of aniline colours should not contain more than 1 per cent. of acetone.

Determination of Acetone.—10 c.c. of $\frac{N}{2}$ caustic soda are poured into a test tube of 50 c.c. capacity, containing 1 c.c. of the sample under examination. 5 c.c. of $\frac{N}{1}$

* *Chemical News,* vol. xlv., p. 152.

iodine are added, and the mixture shaken. The precipitate of iodoform is dissolved in 10 c.c. of ether, and 5 c.c. of the etherial solution are evaporated in a tared watch-glass. The residue represents iodoform, CHI_3, which is calculated to acetone.

METHYL ALKALI BLUE (G.) (O.) (M.) (D. & H.) (B.) (K.) *v.* ALKALI BLUE 6 B (S.C.I.).

METHYLATED SPIRITS *v.* ALCOHOL.

METHYL BLUE (C.) *v.* BAVARIAN BLUE D B F.

METHYL BLUE FOR COTTON (O.) (K.) (M.) *v.* BAVARIAN BLUE D B F.

METHYL BLUE FOR SILK (M.). *Methyl blue soluble in water* (G.), *Marine blue B* (S.C.I.), *Bavarian blue D S F* (Ber.). A rosaniline derivative. *Sodium salt of triphenyl pararosaniline di- and tri-sulphonic acid.* 1862. Dark blue powder, soluble in water. In concentrated H_2SO_4, yellowish-brown solution, which becomes blue on dilution.

Application.—An acid colour. Dyes *silk* bright blue from an acidified soap bath.

METHYL COTTON BLUE *v.* BAVARIAN BLUE D B F.

METHYL DIPHENYLAMINE BLUE (M.). An obsolete basic colour. *Hydrochloride of dimethyltriphenyl pararosaniline.*

METHYLENE BLUE B and B G (B.). *Methylene blue B B, 1 a, D, D extra* (M.) (Ber.), *Methylene blue B B extra* (B.) (M.) (Ber.) (F.), *Methylene blue B B cryst* (M.) (C.R.), *Ethylene blue* (O.). A thiazine derivative. *Hydrochloride or zinc chloride double salt of tetramethyl thionine.*

$$\left(\text{Thionine} = NH_2 \cdot C_6H_3 \!<\!\!\begin{array}{c}S\\N\end{array}\!\!>\! C_6H_3 \cdot NH_2\right).$$

The following are simple *hydrochlorides :*— *Methylene blue B G, B B extra, D, D extra, 1 a.* The following are *zinc chloride double salts:*— *Methylene blue B, B B.* 1876. Dark blue or bronzy powder or crystals, soluble in water. In concentrated H_2SO_4, yellowish-green solution, which becomes blue on dilution. Reducing agents decolorise the aqueous solution, but the colour is readily restored by exposure to air.

Application.—A basic colour. Dyes *wool, silk,* or tannin-mordanted *cotton* blue from a neutral or slightly alkaline bath. *v.* also NEW METHYLENE BLUE.

METHYLENE GREY O, N D, N F (M.). *New methylene grey G and B* (M.), *New grey* (By.), *Nigrisin* (P.), *Malta grey* (P.), *Direct grey J, B, 4 R, R* (P.); *Special grey R* (P.), *Alsace grey* (Fi.). Colours of unknown constitution obtained by boiling a solution of *nitrosodimethylaniline hydrochloride* in water or alcohol. 1885. Greyish-black powders, giving a reddish-grey solution in water. In

concentrated H_2SO_4, greenish solution, which becomes reddish-grey on dilution.

Application.—Basic dyes, which will also dye direct. Dye unmordanted or tannin-mordanted *cotton* various shades of grey.

METHYLENE GREEN EXTRA YELLOW, G, CONCENTRATED (M.). *Mononitro compound of methylene blue.* 1886. Dark brown powder, soluble in water with a greenish-blue colour. In concentrated H_2SO_4, dark green solution, which becomes blue on dilution.

Application.—A basic dye. Dyes tannin-mordanted *cotton* dark green. Chiefly used in *calico* printing.

METHYLENE VIOLET 2 R A and 3 R A (M.) *v.* FUCHSIA (S.C.I.).

METHYL EOSIN (Mo.) (S.C.I.) *v.* PRIMROSE (D. & H.).

METHYL EOSIN (Ber.) *v.* EOSIN B N (B.).

METHYL GREEN (By.) (Ber.) (K.). *Vert etincelle* (Mo.), *Double green S F* (K.), *Light green, Paris green.* A rosaniline derivative. *Zinc chloride double salt of heptamethyl pararosaniline chloride.* 1871. Green crystals, easily soluble in water. In concentrated H_2SO_4, reddish-yellow solution, which becomes yellowish-green on dilution.

Application.—A basic colour. Dyes *silk* or tannin-mordanted *cotton* green from a neutral bath.

METHYL GREEN (By.) (Ber.) (P.). *Ethyl green.* A rosaniline derivative. *Zinc chloride double salt of ethyl hexa-methyl pararosaniline bromide.* 1866. Moss-green crystalline powder, easily soluble in water. In concentrated H_2SO_4, yellow solution, which becomes green on great dilution.

Application.—A basic colour. Dyes *wool* mordanted with sulphur or zinc, *silk* or *cotton* mordanted with tannin, bluish-green.

METHYL ORANGE *v.* ORANGE III.

METHYL ORANGE (indicator) *v.* ACIDIMETRY.

METHYL VIOLET B and 2 B (all makers). *Methyl violet V 3* (K.), *Violet de Paris* (P.), *Dahlia.* A rosaniline derivative. Chiefly *hydrochloride of penta- and hexamethyl pararosaniline.* 1861. Glistening metallic green lumps or powder, easily soluble in water or alcohol. In concentrated H_2SO_4, yellow solution, which becomes first yellowish-green, then greenish-blue, blue, and finally violet on dilution.

Application.—A basic colour. Dyes *wool, silk,* or tannin-mordanted *cotton,* violet. Used also in preparing copying inks for the gelatine pad process; also for ink pencils, &c.

METHYL VIOLET 6 B and 6 B EXTRA (all makers). *Methyl violet 7 B, Violet 5 B, 6 B, 7 B, Benzyl violet, Paris violet 6 B, 7 B.* A rosaniline derivative obtained by the benzylation of methyl violet B. Chiefly *hydro-*

chloride of benzyl penta- and hexa-methyl pararosaniline. 1868. Brown metallic glistening lumps or powder, similar in reactions, properties, and uses to *Methyl violet B*.

METHYL WATER BLUE (B.) *v.* Bavarian Blue DBF.

MEXICAN BLUE is the colouring matter of *Sericographis mohite*, and dyes *wool* and *cotton* purplish-blue without mordant.

MIKADO BROWN B, 4G O, and M (L.). Colours of unknown constitution obtained by the action of alkalies and oxidising agents upon *para-nitro toluol sulphonic acid*. 1888. Brown powders, soluble in water. In concentrated H_2SO_4 they give reddish-black to blue-black solutions, which on dilution give a brown ppt.
Application. — Direct cotton dyes. Dye *cotton* bluish to yellowish-brown from a salt bath.

MIKADO GOLD YELLOW 2G, 4G, 6G, 8G (L.). *Direct yellow 2 G, 3 G* (K.). Nitro colours. *Sodium salts of dinitro stilbene disulphonic acid.* 1886. Yellow powders, soluble in water. In concentrated H_2SO_4 they give orange to red solutions, which become yellow on dilution.
Application.—Direct cotton colours. Dye *cotton* bright yellow from a salt bath.

MIKADO ORANGE G, R, 2R, 3R, 4R, 5 R, and Mikado Yellow (L.). Colours of unknown constitution obtained in the same way as *Mikado brown.* 1888. Orange to red powders, soluble in water. In concentrated H_2SO_4, red to blue solutions are obtained, which give brown ppts. on dilution.
Application.—Direct cotton colours, which dye *cotton* reddish-orange to yellow from a salt bath.

MIKADO YELLOW. *v.* above.

MILLING BLUE (K.). An azine derivative. 1890. Bronze powder, soluble in water with a blue colour. Concentrated H_2SO_4, blue-green solution; on dilution, blue.
Application.—A mordant dye, giving blue shades on chrome-mordanted *wool*.

MILLING GREEN (D.). 1893. An acid colour, giving bluish-greens on *wool*.

MILLING GREEN, S (L.). 1898. An acid dye, producing very fast colours on *wool*.

MILLING ORANGE (D.). An azo dye.

Amidoazo benzol disul- — *Salicylic acid.*
phonic acid

Red-brown powder, giving an orange-red solution in water. Concentrated H_2SO_4, violet solution; on dilution, greyish-yellow ppt.
Application.—An acid mordant dye. Dyes chrome-mordanted *wool* orange-red.

MILLING RED B, F F G, G, F R, R (C.). Mark G. Red powder. Aqueous and alcoholic solution, yellowish-scarlet. Concentrated H_2SO_4, purple solution; on dilution becomes scarlet.
Application.—Acid mordant colours. Dye direct from acid bath or on chrome-mordanted *wool*, giving bright red shades.

MILLING SCARLET (Br.S.) *v.* Acid and Milling Scarlet.

MILLING YELLOW (D.) *v.* Mordant Yellow (B.).

MILLING YELLOW O O (C.) is a monazo dye.
Application.—An acid colour. Dyes unmordanted *wool* bright yellow.

MILK OF LIME *v.* Calcium Hydroxide.

MIMOSA (G.). Obtained by the action of *ammonia upon diazotised primuline.* 1890. Yellowish-brown powder, soluble in water. In concentrated H_2SO_4, yellow solution.
Application.—A direct cotton colour. Dyes *cotton* yellow from a salt bath.

MINERAL OILS *v.* Lubricating Oils.

MINIUM *v.* Lead Tetroxide.

MORDANT DYES. The common characteristic of these dyestuffs is their ability to form, with metallic oxides, insoluble lakes which can be fixed on the textile fibres; but in other respects they differ greatly in their behaviour. Some cannot be dyed at all without the aid of mordants, and cannot be considered as true colours, but rather as colouring principles which yield the coloured body only in combination with metallic oxides. Of these substances some produce, with the different oxides, one colour only, or at most various shades of a colour; others yield a great variety of colours (*e.g., alizarin*). Others, again, are more or less capable of dyeing the textile fibres without mordants—*e.g., alizarin blue, alizarin yellow, &c.*, and *cloth red.*

The mordant dyes may be divided into the following classes:—(a) *Alizarins*, (b) *Derivatives of pyrogallol*, (c) *Azo compounds*, (d) *Nitroso compounds*.

The first class, comprising the alizarins, contains the double ketone group $\left\{ \begin{matrix} CO \\ CO \end{matrix} \right\}$ as chromophor, and, as auxochromous groups, two hydroxyl molecules (OH groups) in ortho-position to each other, one of them being in orthoposition to one of the CO groups.

The second class consists of derivatives of pyrogallol (or gallic acid), which also contain two or more hydroxyl molecules in ortho-position to the chromophor. *Coeruleïn* may also be included among the members of this class.

The third class consists of azo compounds, which are either derivatives of salicylic acid, or of naphthol sulphonic acid, or of substances of unknown chemical constitution (*e.g., patent fustin*).

The fourth and last class consists of nitroso compounds and others of analogous consti-

tution. These substances differ chemically and tinctorially from the preceding classes. v. DARK GREEN.

The mordant dyes are used in dyeing and printing cotton, linen, wool, and silk, and are employed in constantly increasing quantities on account of the great fastness they exhibit to soaping and milling. As a rule, they are very fast to light and resist well most chemical agents, such as sulphur dioxide, chlorine, acids or alkalies; in short, they are among the fastest colours known. It will be noticed that most of the natural colouring matters which are distinguished for fastness are mordant colours—e.g., logwood and *fustic*. *Indigo* in common with some artificial dyestuffs, such as *indophenol* and *aniline black*, form exceptions to the rule that fast colours are mordant colours.

Dyeing with mordant dyes is accomplished, as a rule, by one of two methods :—(1) Mordanting; (2) dyeing (mordanting and dyeing method). Both operations may, in some cases, be combined in one bath (single-bath method), while sometimes their order is inverted by first dyeing or "stuffing," and subsequently fixing or "saddening" with the mordant (dyeing and saddening method).

Various sesquioxides, principally those of *aluminium, chromium,* and *iron,* and *stannous* and *stannic oxides,* are used as mordants, oxides of other metals being of minor importance. *Chromic oxide* is the mordant employed with the greatest number of these colours, while *aluminium oxide* yields the most brilliant shades, as, for example, "Turkey-red." The principal mordant for the *nitroso compounds* is *ferric oxide;* for other colours it is not frequently used, except for the production of very fast shades of violet, with the aid of alizarin.

Most mordant colours can be mixed and dyed in the same bath, provided they are fixed by the same mordant; colours requiring different mordants cannot with advantage be used for the production of mixed shades in one bath.

The mordant dyes frequently behave as mordants towards the basic colours, the latter being sometimes used to brighten or to shade a mordant colour, either by adding the basic colour to the dye-bath or by subsequent topping.

The mordant colours, which are readily soluble in water and are sold in the form of powder, are added to the dye-bath in the

---

MORDANT DYES (For Names of Makers see Alphabetical Description of Colours).

Reds.

Alizarin (various marks).
Alizarin Bordeaux.
    ,,   Cardinal.
    ,,   Maroon.
    ,,   Powder S, 3 S, W S,
              &c.
    ,,   Purpurin.
Anthrapurpurin.
Chrome Bordeaux.
    ,,   Red.
    ,,   Rubine.
Flavopurpurin.
Purpurin.

Oranges.

Alizarin Orange.
Diamond Orange.

Yellows.

Alizarin Yellows.
Anthracene Yellows.
Azochromine.
Chrome Fast Yellow 2 G, G,
              R.
    ,,   Yellow B.
Diamond Flavin.
    ,,   Yellow B, G, R.
Flavazol.
Fustine.
Galloflavin.

Gambine Yellow.
Milling Yellow.
Mordant Yellow O, R.
Prague Alizarin Yellow.
Resoflavin.

Greens.

Acid Alizarin Green.
Alizarin Cyanin Green.
    ,,   Dark Green.
    ,,   Green B, G, S W.
    ,,   Viridine.
Coeruleïn A, B, S, S W.
Dark Green.
Gambine B, R, Y.
Naphthol Green B.

Blues.

Acid Alizarin Blue 2 B, G R.
Alizarin Blues.
    ,,   Cyanins.
    ,,   Dark Blue.
    ,,   Indigo Blue S W.
    ,,   Sapphirole.
Anthracene Blues.
    ,,   Dark Blue W.
Brilliant Alizarin Blue G, D,
              R.
    ,,   ,,   Cyanin G.
Celestine Blue.
Chrome Blue.
Chromocyanine.

Delphin Blue.
Gallamine Blue.
Phenocyanine B, R, T V, T B.

Violets.

Alizarin Heliotrope R.
Azogalleïn.
Chrome Prune.
    ,,   Violets.
Galleïn.
Gallocyanin.
Solid Violet.

Blacks.

Alizarin Blacks.
    ,,   Cyanin Black G.
Anthracene Acid Black L W,
              S T.
    ,,   Chrome   Black,
              F, F E, 5 B.
Diamond Blacks.

Browns.

Alizarin Browns.
    ,,   Red Brown.
Anthracene Acid Brown B,
              G, N, R.
    ,,   Browns.
Chrome Browns.
Diamond Browns.
Rufigallol.
Sulphamin Brown.

solution. With the exception of the bisulphite compounds, they may be dissolved in boiling water. The latter, however, are decomposed by hot water, so that the water for this purpose should be cold, or, at most, lukewarm. Many of the mordant colours are sold as "sparingly soluble" pastes; these are mixed with a little water, and passed, through a fine sieve, into the dye-bath; they are thus in a state of fine division and gradually dissolve in the dye-liquor.

MORDANTS. This term is often erroneously used to designate any substance other than the colouring matter itself, which is used in the dye-bath. Thus the sulphuric acid and sodium sulphate employed in the acid dye-bath are by some termed "mordants," but this is a misuse of the term, which should indeed be confined to those substances which combine with the colouring matter employed and form an integral part of the colour as fixed on the material.

Mordants are not by any means invariably necessary, many dyestuffs being capable of fixing themselves upon some or all textiles without their intervention. Thus the *acid, basic,* and *direct cotton* dyes all dye wool without the aid of mordants, but the *mordant dyes* do not possess this property, and must be used in conjunction with mordants whatever the nature of the fibre to which they are applied. The *basic* dyes, however, which dye wool direct, must be used along with mordants in cotton dyeing.

It will thus be seen that the necessity for the use of a mordant depends partly upon the nature of the colouring matter and partly upon the fibre under treatment.

There are two distinct classes of mordants, differing entirely in their chemical character. The *metallic mordants* are used in conjunction with dyes which contain in their molecule either *hydroxyl* (OH) or *carboxyl* (COOH) groups, while the *acid mordants* (of which tannic acid is much the most important) are employed with the so-called *basic colours* which are *amidic* in character.

The group of "mordant dyes," for which metallic mordants are essential, includes most of the natural colouring matters, such, for example, as *logwood, madder, fustic,* and *cochineal,* the chief exceptions being *indigo, orchil,* and *turmeric.* To this group also belongs the important class of artificial dyes known as the "alizarin" dyes, as well as others (v. MORDANT DYES).

The metallic mordants chiefly used are salts of *chromium, iron, aluminium, tin,* and *copper,* although compounds of *zinc, nickel, cobalt, uranium,* and other metals are employed for special purposes. The table below gives a *résumé* of the particular metallic salts commonly used in wool, silk, and cotton dyeing.

The function of the metallic mordants is not merely to *fix* the colour on the fibre, but also to aid in its *production.* Most of the metallic mordants and all the mordant dyes are coloured substances, but the colour of the bodies has nothing whatever to do with

MORDANTS EMPLOYED FOR THE DIFFERENT FIBRES.

	Wool.	Silk.	Cotton.
Chromium, . .	Bichromates of potash and soda. Chrome alum. Chromium fluoride.	Basic chromic salts. Chromium chromates.	Bichromates. Basic chromic salts. Chromium chromates. Chromium bisulphite.
Iron, . . .	Ferrous sulphate.	Bassic ferric sulphate and nitrate. Ferrous acetate (Pyrolignite).	Basic ferric sulphate. Ferrous acetate. Ferrous sulphate.
Aluminium, . .	Potassium or ammonium alum. Aluminium sulphate.	Basic alum.	Basic alum. Aluminium acetate.
Tin, ...	Stannous chloride.	....	....
Copper, . . .	Cupric sulphate.	Cupric sulphate.	Cupric sulphate. Cupric acetate.
Zinc, . . .	Zinc sulphate.	....	....
Nickel, . . .	Nickel sulphate.	....	....
Cobalt, . . .	Cobalt sulphate.	....	....
Uranium, . .	Uranyl sulphate.	....	....

the colour of the new compound which is formed on the fibre. For example, bichromate of potash is orange coloured and logwood is brown, but the colour produced on the fibre is blue or black. Again, stannous chloride is colourless and cochineal dull maroon, but their combination yields a brilliant scarlet. The ultimate colour also depends quite as much on the nature of the mordant as on the colouring matter; *e.g.*, cochineal with iron mordant produces a purplish-grey or black.

The *acid mordants* are of less importance. Practically they are only employed in the fixation of the basic dyes on cotton, and partake indeed more of the character of fixing agents than of true mordants, since they are essential only to the *fixation* and not to the *production* of the colour, which as fixed upon the fibre is almost identical in colour with the dyestuff itself.

Tannic acid is the chief acid mordant (*v.* TANNIN MATTERS and TANNIC ACID). *Oleic acid, soap,* and *sulphated oil* are also used.

MORDANT YELLOW (B.). *Mordant yellow O* (M.), *Chrome yellow D* (By.), *Milling yellow* (D.), *Anthracene yellow B N* (C.). An azo dye.

$$\frac{Beta\text{-}naphthylamine}{sulphonic\ acid\ Br} - Salicylic\ acid.$$

1890. Yellow powder, soluble in water with a yellowish-red colour. In concentrated H_2SO_4, orange-red solution, which, on dilution, precipitates reddish-grey flocks.

Application.—An acid-mordant dye. Dyes chrome-mordanted *wool* yellow.

MORDANT YELLOW R (B.). 1897. A somewhat redder shade than the above.

MORIC ACID *v.* FUSTIC (OLD).

MORIN *v.* FUSTIC (OLD).

MORITANNIC ACID *v.* FUSTIC (OLD).

MOSAIC GOLD *v.* STANNIC SULPHIDE.

MUNJEET is the root of *Rubia munjista* (*cordifolia*). It is closely allied to *Madder*, but is peculiar in that it contains *purpurin* only, and on this account produces somewhat duller and less permanent shades than madder. It is an important Indian dyestuff.

MUREXIDE. *Naples red.* An obsolete red basic dye, obtained by the action of nitric acid on guano, and subsequently treating the product with ammonia.

MURIATE OF AMMONIA *v.* AMMONIUM CHLORIDE.

MURIATE OF IRON *v.* IRON (FERROUS CHLORIDE).

MURIATIC ACID *v.* HYDROCHLORIC ACID.

MUSCARINE (D. & H.). *Campanulin* (Ber.). An oxazine derivative. *Chloride of dimethylphenyl para - ammonium beta - oxy - naphthoxazine.* 1885. Brownish - violet

powder, slightly soluble in cold water. In concentrated H_2SO_4, bluish-green solution, which becomes first blue, then violet, and finally gives a violet ppt. on dilution.

Application.—A basic colour. Dyes tannin-mordanted *cotton* blue.

MYRABOLAMS. These are, perhaps, more largely used in cotton dyeing than any other form of tannin. They are the fruit of several species of *Terminalia*, growing principally in China and the East Indies. They are imported in the dried condition, and are extremely hard and tough, brown in colour, and about an inch long. The stone in the interior of the fruit, which constitutes about 25 per cent. of the weight of the fruit, contains little tannin, but the whole fruit, when ground together, averages 25 to 40 per cent. The principal tannin in myrabolams is *ellagitannic acid*, and there is also present a considerable amount of yellowish-brown colouring matter, which is still more objectionable than the sumac colouring matter as a basis for pale shades.

MYRTLE GREEN *v.* DARK GREEN.

N

NANKIN YELLOW *v.* IRON BUFF.

NANKIN YELLOW *v.* PHOSPHINE.

NAPHTHALENE, $C_{10}H_8$, occurs in coal tar. It crystallises and sublimes in colourless glittering laminæ; melts at 79° C., and boils at 218° C. It possesses a peculiar smell. Naphthalene is insoluble in water, sparingly soluble in cold alcohol, and freely soluble in ether or hot alcohol. It evolves large quantities of dense black smoke when burning in the air.

NAPHTHALENE BLUE B (M.).⎫ 1889. Acid dyes for wool.

NAPHTHALENE GREEN V, concentrated (M.).⎬

NAPHTHALENE RED ⎫ *v.* MAGDALA RED.

NAPHTHALENE ROSE ⎬

NAPHTHALENE SCARLET ⎭

NAPHTHALENE YELLOW *v.* MARTIUS YELLOW.

NAPHTHAZARIN S *v.* ALIZARIN BLACK S.

NAPHTHAZINE BLUE (D.) (M.). An azine derivative. *Sodium salt of beta-naphthyl dimethyl beta-naphthyl safranine sulphonic acid.* 1892. Glistening bronze powder, soluble in water with a blue colour. In concentrated H_2SO_4, blue-green solution, becoming blue on dilution.

Application.—An acid colour. Dyes *wool* dark blue from an acid bath.

NAPHTHAZURIN B, 2B, and R (O.). Basic dyes. Giving navy-blue shades on tannin-mordanted *cotton*.

NAPHTHINDONE 2 B (C.). Brown powder. Aqueous and alcoholic solution reddish-

blue. Concentrated H_2SO_4, olive-green solution; on dilution, reddish-blue.

Application.—A basic dye. Dyes tannin-mordanted *cotton* blue. Used also in *calico* printing.

NAPHTHIONIC ACID, $C_{10}H_6(NH_2)$ (SO_3H), $(1:4)$, is the alpha-sulphonic acid of alpha-naphthylamine. It was discovered by Piria, and is prepared by heating alpha-naphthylamine sulphate (Neville and Winther).

NAPHTHION RED *v.* Orchil Extract V.

NAPHTHOCYANINE. An obsolete direct cotton blue dye.

NAPHTHOL and NAPHTHYLAMINE COMPOUNDS.

Alpha-Naphthol, $C_{10}H_7OH$, (OH : 1). Alpha-naphthol is obtained by fusing sodium alpha-naphthalene sulphonate (1 part) with caustic soda (2 to 3 parts) and a little water at 270° to 300° C. in an iron pot provided with a mechanical stirrer. The sodium naphtholate which rises to the surface is removed, dissolved in water, and decomposed with hydrochloric or carbonic acid. The precipitated alpha-naphthol is dried and purified by distillation.

Properties.—Alpha-naphthol crystallises in lustrous monoclinic needles, sparingly soluble in hot water, but readily soluble in caustic alkalies, forming salts (naphtholates). It melts at 94° C., and boils at 278° to 280°. It has a phenolic odour, and volatilises readily with steam. It is soluble in alcohol, ether, chloroform, and benzene. With chloride of lime it produces a dark violet colour and precipitate, and likewise with ferric chloride.

Uses.—Alpha-naphthol is chiefly used in the manufacture of naphthol yellow. It also forms the *maroon* developer in dyeing with primuline.

Examination.—Commercial alpha-naphthol occurs in the form of white crystalline lumps. Its melting point should be near that of pure alpha-naphthol. It usually contains a little beta-naphthol, the presence of which may be inferred and the amount approximately estimated by comparing the melting point with that of standard mixtures of pure alpha- and beta-naphthol. The sample should dissolve almost completely in caustic soda.

Alpha - Naphthylamine, $C_{10}H_7NH_2$, $(NH_2 : 1)$, is obtained by the reduction of alpha-nitronaphthalene with iron borings and hydrochloric acid.

Properties.—It forms flat colourless needles or plates, melting at 50° C., and boiling at 300°. It is almost insoluble in water, but readily soluble in alcohol or ether. With acids it combines to form well-defined salts, the aqueous solutions of which yield with mild oxidising agents a blue precipitate of naphthameïn. It possesses a characteristic and very disagreeable odour.

Uses.—Alpha-naphthylamine is used in the manufacture of azo dyes, naphthol yellow, and magdala red. It is also used as a *brown* developer in the dyeing of primuline colours.

Examination. — The commercial product forms greyish-white or brownish crystalline lumps. Its melting point should be very nearly the same as that of the pure compound, and it should dissolve almost completely in dilute hydrochloric acid. Small quantities of naphthalene are usually present, the proportion of which can be determined by distilling a large quantity of the sample with excess of hydrochloric acid in a current of steam, extracting the distillate with ether, and, after drying the etherial solution, evaporating and weighing the residue.

Alpha-Naphthol Sulphonic Acid (N.W.), $(C_{10}H_6)(OH)(SO_3H)$, is obtained from naphthionic acid, and was first prepared by Neville and Winther.

This is one of the seven isomeric α-naphthol monosulphonic acids, most of which are used in colour making.

Alpha-Naphthol Disulphonic Acid (Sch.), $(C_{10}H_5)(OH)(SO_3H)_2$, is prepared by boiling the diazo compound of α-naphthylamine disulphonic acid with water, and is one of ten isomeric disulphonic acids of α-naphthol.

Dioxy - Naphthalene Sulphonic Acid, $C_{10}H_5(OH)_2(SO_3H)$, is obtained by heating alpha-naphthol disulphonic acid (Sch.) with caustic soda.

Alpha-Naphthylamine Sulphonic Acid (L.), $C_{10}H_6(NH_2)(SO_3H)$, was discovered by Laurent, and is one of seven isomeric acids.

Alpha-Naphthylamine Disulphonic Acid, $C_{10}H_5(NH_2)(SO_3H)_2$. Prepared by the action of fuming sulphuric acid on alpha-naphthylamine, and is a mixture of several isomeric compounds.

Beta-Naphthol, $C_{10}H_7(OH)$; (OH : 2), is obtained analogously to alpha-naphthol by fusing beta-naphthalene monosulphonic acid with caustic soda. It crystallises in colourless, glittering laminæ, melts at 122° C., and boils at 286° C. It is sparingly soluble in hot water, readily in alcohol and ether. The aqueous solution becomes greenish on addition of ferric chloride. Beta-naphthol also resembles the phenols in forming salts (naphtholates), and dissolving in caustic soda.

Verhassel * gives the following test for distinguishing α from β-naphthol.

The *azo compounds* of beta-naphthol are essentially different from those of alpha-naphthol. They possess in the non-sulphonated state a slightly basic character, and containing no hydroxyl group, are not soluble in caustic soda.

* *Chem. News*, vol. lxvi., p. 220.

Reagent.	α-Naphthol in Aqueous Solution.	β-Naphthol in Aqueous Solution.
Chloride of lime, . .	A violet coloration.	Turns greenish-yellow.
Potassium ferrocyanide, .	,, ,,	,, light yellow.
Potassium ferricyanide, .	A brown coloration.	Greenish-yellow.
Ammonia, ...	Remains colourless in alcoholic solution.	Greenish coloration in alcoholic solution.
Ferric chloride, . .	A violet precipitate.	Greenish coloration and precipitate.

Dioxy-Naphthalenes, $C_{10}H_6(OH)_2$. — A great number of these are known.

Beta-Naphthylamine, $C_{10}H_7NH_2$; $(NH_2 : 2)$, is prepared by heating beta-naphthol with ammonia. It forms colourless inodorous laminæ, melts at 112° C., and boils at 294° C. It is sparingly soluble in cold, but freely soluble in hot water, alcohol, and ether. The commercial product is very pure, and forms a fused pink-coloured mass.

Beta-naphthylamine is a monacid base, and forms crystalline salts.

The hydrochloride $(C_{10}H_7NH_2 . HCl)$ is fairly soluble in water.

Beta-Naphthol Mono-sulphonic Acid (S), $C_{10}H_6(OH)(SO_3H)$, is known as *Schaeffer's acid*, and is one of seven isomeric acids.

Beta-Naphthol Disulphonic Acid R (*R. Salt*), $C_{10}H_5(OH)(SO_3H)_2$, is one of several isomeric acids.

Beta-Naphthylamine Alpha-Sulphonic Acid, $C_{10}H_6(NH_2)_2(SO_3H)$, is one of several isomeric acids, distinguished as alpha, beta, &c.

Beta-Naphthylamine Disulphonic Acid (R.), $C_{10}H_5(NH_2)(SO_3H)_2$ (*Amido R acid*), is produced by the action of ammonia on R salt, and may be taken as a type of several isomeric compounds.

Gamma-Amidonaphthol Sulphonic Acid, $C_{10}H_5(NH_2)(OH)(SO_3H)$, is produced by heating amido G acid with caustic soda.

NAPHTHOL BLACK B (C.). *Brilliant black B* (B.). An azo dye.

Alpha-naphthyl- < *Beta-naphthylamine.*
amine < *Beta-naphthol disulphonic acid R.*

1885. Blue-black powder, soluble in water with a violet colour. In concentrated H_2SO_4, green solution, which on dilution becomes bluer and then deposits a violet ppt.

Application.—An acid colour. Dyes *wool* blue-black from an acid solution.

NAPHTHOL BLACK 6 B (C.) (D.). An azo dye.

Alpha-naphthyl- < *Alpha-naphthylamine disulphonic.*
amine < *Beta-naphthol disulphonic acid R.*

1885. Black powder, giving a violet solution in water. In concentrated H_2SO_4, greenish-black solution, which on dilution first becomes green and then gives a violet ppt.

Application.—An acid colour. Dyes *wool* bluish-black from an acid bath.

NAPHTHOL BLACK 3 B, 12 B (C.). Similar to the above.

NAPHTHOL BLUE G, R (C.). Acid dyes, producing dark navy blue shades on *wool*.

NAPHTHOL BLUE B *v.* NEW BLUE.

NAPHTHOL BLUE D and R *v.* NEW BLUE R.

NAPHTHOL BLUE-BLACK (C.). An azo dye.

Amidonaphthol disul- < *Para-nitraniline.*
phonic acid H < *Aniline.*

1891. Black powder, soluble in water with a blue-black colour. In concentrated H_2SO_4, green solution ; on dilution, blue ppt.

Application.—An acid dye. Dyes *wool* blue-black from an acid bath.

NAPHTHOL GREEN B (C.). A nitroso compound. The *iron compound of nitroso beta-naphthol sulphonate of soda*. 1883. Dark green powder, soluble in water with a yellowish-green colour. In concentrated H_2SO_4, yellowish-brown solution, which becomes yellow on dilution, and gives a precipitate of Prussian blue with potassium ferro- or ferri-cyanide.

Application.—An acid mordant dye. Dyes *wool* dark green from a bath containing ferrous sulphate and sulphuric acid.

NAPHTHOL ORANGE (Ber.) *v.* ORANGE I.

NAPHTHOL RED 0 (M.) *v.* AMARANTH (M.).

NAPHTHOL RED S (M.) *v.* AMARANTH (M.).

NAPHTHOL SCARLET 3 R (D.). A bright acid red dye.

NAPHTHOL YELLOW *v.* MARTIUS YELLOW.

NAPHTHOL YELLOW S (B.) (By.) (C.) (C.R.) (D. & H.) (S.C.I.) (M.) (Lev.) (O.). *Citronine A* (L.), *Acid yellow* (D. & H.), *Sulphur yellow S* (K.). A nitro compound. *Sodium or potassium salt of dinitro alpha-*

naphthol sulphonic acid. 1879. Orange-yellow powder, soluble in water. In concentrated H_2SO_4, light yellow solution; on dilution, slightly greener. Deflagrates on heating.

Application.—An acid colour. Dyes *wool* or *silk* greenish-yellow from an acid bath.

NAPHTHOL YELLOW R S (By.) *v.* BRILLIANT YELLOW (Sch.).

NAPHTHYLAMINE COMPOUNDS *v.* NAPHTHOL.

NAPHTHYLAMINE BLACK 4 B (C.). Black powder. Aqueous and alcoholic solution, reddish-blue. Concentrated H_2SO_4, greenish-blue; on dilution, becomes blue.

Application.—*v.* NAPHTHYLAMINE BLACK D.

NAPHTHYLAMINE BLACK 6 B (C.). Violet-black powder. Aqueous solution, bright blue; alcoholic solution, reddish-blue. Concentrated H_2SO_4, bluish-green; on dilution, becomes reddish-blue.

Application.—*v.* NAPHTHYLAMINE BLACK D.

NAPHTHYLAMINE BLACK D (C.). An azo dye.

Alpha-naphthyl-amine $\Big\langle$ *Alpha-naphthylamine.*
Alpha-naphthylamine disulphonic acid.

1888. Black powder, soluble in water, with a violet-black colour. In concentrated H_2SO_4, greenish-black solution; on dilution, first greenish-blue solution, then violet ppt.

Application.—An acid colour. Dyes *wool* blue-black from an acid bath.

NAPHTHYLAMINE BROWN (B.). *Fast brown N* (B.), *Azo brown O* (M.), *Chrome brown R O* (M.). An azo compound.

Naphthionic acid — Alpha-naphthol.

1878. Brown powder, giving a yellowish-brown solution in water. In concentrated H_2SO_4, violet solution; on dilution, magenta-red solution.

Application.—An acid colour. Dyes *wool* orange-brown from an acid bath. If oxidised with bichromate of potash after dyeing, the colour is fast to alkalies and acids.

NAPHTHYLAMINE RED (D. & H.) *v.* MAGDALA RED.

NAPHTHYLAMINE YELLOW (K.) *v.* MARTIUS YELLOW.

NAPHTHYL BLUE (K.). A sulphonated form of *Milling blue* (K.). An acid colour, dyeing *silk* violet-blue with red fluorescence. Fast to light.

NAPHTHYL BLUE 2 B (B.). An azo dye.

Orthodiamido diphenic acid $\Big\langle$ *Benzoyl amidonaphthol sulphonic acid.*
Benzoyl amidonaphthol sulphonic acid.

1890. Dark blue soluble powder. In concentrated H_2SO_4, bright blue solution; on dilution, violet ppt.

Application.—A direct cotton colour. Dyes *cotton* pure blue from a salt bath.

NAPHTHYL BLUE BLACK N (C.). Brownish-black powder. Aqueous solution, reddish-blue; alcoholic solution, slightly bluer. Concentrated H_2SO_4, bluish-green solution; on dilution, becomes reddish-blue.

Application.—An acid dye. Gives dark navy-blue shades on *wool.*

NAPHTHYLENE BLUE R cryst. (By.) *v.* NEW BLUE R.

NAPHTHYLENE RED (B.). An azo dye.

Diamido naphthalene $\Big\langle$ *Naphthionic acid.*
Naphthionic acid.

1886. Brownish-red powder, giving a red solution in water. In concentrated H_2SO_4, blue solution; on dilution, blue-black ppt.

Application.—A direct cotton colour. Dyes *cotton* red from an alkaline bath.

NAPHTHYL VIOLET (K.). An acid dye.

NAPHTORUBIN (By.) (M.) *v.* PALATINE RED (B.).

NAPLES RED *v.* MUREXIDE.

NARCEÏN (D. & H.). A hydrazo compound obtained by combining *azobenzene sulphonic acid with beta-naphthol* and treating the product with *sodium bisulphite.* 1879. Reddish-yellow powder, easily soluble in water. In concentrated H_2SO_4, yellowish-brown solution, which evolves sulphurous acid on dilution and warming.

Application.—An acid dye. Dyes *wool* orange from an acid bath. Used in *wool* printing.

NATURAL COLOURING MATTERS. Colouring matters, or, more correctly speaking, the colouring principles from which they are derived, are very widely distributed in the vegetable kingdom. Very few natural colouring matters were, however, practically employed in dyeing, even before the competition of the coal-tar colours relegated many of them to the museum. The following short list almost exhausts them.

NATURAL DYESTUFFS IN GENERAL USE PRIOR TO 1860.

Logwood.	Old Fustic.
Madder.	Weld.
Peachwood.	Quercitron Bark.
Camwood.	Young Fustic.
Barwood.	Persian Berries.
Saunderswood.	Catechu.
Cochineal.	Turmeric.
Indigo.	Sumac and Gall Nuts.
Orchil and Cudbear.	

Each of these will be found described under their respective names.

A few others were employed for special purposes—such as, annatto, safflower, barberry bark, green ebony, saffron, &c.—but making due allowance for these, it is evident that the total number was extremely small.

The development in this respect has, moreover, been very slow, as is shown by the following list of

DYESTUFFS IN USE IN EUROPE IN 1600.

Indigo.	Buckthorn.
Woad.	Lac-Dye.
Madder.	Kermes.
Litmus.	Young Fustic.
Brazilwood.	Catechu.
Archil.	Sumac and Gall Nuts.

Natives of other countries where the textile arts have attained any great development—notably, Persia, India, and Japan—have each their own series of indigenous vegetable products from which they obtain dyes, and the number of these is greatly in excess of the number at any time used in Europe. The reason for our limited selection is not far to seek. None of our native plants are of much commercial value as dyestuffs, practically all the latter are imported, and only those which can be obtained regularly in large quantity and, at the same time, contain a relatively large amount of colouring matter in proportion to their bulk are suitable for the immense requirements of the trade.

As already mentioned, however, the property of yielding colouring matters is almost universal in the vegetable kingdom, and it is interesting to remember that in any garden, wood, or hedgerow, it is possible to gather plants which might serve at a pinch as dye materials, and anyone who wishes to spin, dye, and weave his own raw material at his own fireside need not go far afield for his colouring matters.

In Donegal, Sutherland, and other localities where "Home Industries" associations flourish, the goods chiefly produced being homespun tweeds, hosiery, and underwear, the manufacture is carried on in most primitive fashion, the operations of spinning and weaving being conducted entirely by hand. The dyeing also, until recently, was entirely dependent upon the various lichens, roots, barks, nuts, &c., found in the neighbourhood. Some of the commonest colouring matters in nature cannot, however, be used as dyes, since there is no known method of fixing them on textile fibres in a satisfactory manner. The most notable instance of this is found in *chlorophyl*, the green colouring matter of plants. It is, indeed, interesting to note that, when using natural dyes, green must always be obtained by a mixture of blue and yellow.

NEBLAH v. BABLAH.

NEPTUNE GREEN S (B.). Blue powder. Aqueous and alcoholic solution, bright blue. Concentrated H_2SO_4, yellow solution; on dilution, becomes brownish-yellow, then green, and finally blue.

Application.—An acid dye, giving bright bluish-green shades on *wool*.

NEROGENE D (Ber.). A developer for ZAMBESI BLACKS.

NEROL B, 2 B (Ber.). 1889. Acid dyes, giving blacks on unmordanted *wool*.

NESSLER'S SOLUTION v. AMMONIA.

NEUTRAL BLUE (C.). An azine derivative. *Dimethyl isorosinduline chloride.* 1882. Brown powder, giving a violet solution in water. In concentrated H_2SO_4, brownish-violet solution, becoming violet on dilution.

Application.—A basic colour. Dyes tannin-mordanted *cotton* blue.

NEUTRAL GRAY G (Ber.). Black powder. Slightly soluble in water to blue solution. Alcoholic solution, bluish-red. Concentrated H_2SO_4, blue solution; on dilution, becomes reddish-violet.

Application.—A direct cotton dye.

NEUTRAL RED (C.). *Toluylene red.* An azine derivative. *Dimethyl diamidotolyl phenazine chloride.* 1879. Blackish-green powder, giving a red solution in water. In concentrated H_2SO_4, green solution; on dilution, blue, then magenta-red.

Application.—A basic colour. Dyes tannin-mordanted *cotton* bluish-red.

NEUTRAL VIOLET (C.). An azine derivative. *Dimethyl diamido phenazine chloride.* 1879. Greenish-black paste, which when shaken greatly irritates the mucous membranes. Soluble in water with a violet-red colour. In concentrated H_2SO_4, green solution, which becomes first blue, and then violet on dilution.

Application.—A basic colour. Dyes tannin-mordanted *cotton* reddish-violet.

NEW BLUE B (C.) (S.C.I.). *Fast blue 2 B for cotton* (Ber.) (O.), *Metamine blue B and G* (L.), *Fast marine blue R M, G M* (K.), *New cotton blue B* (M.), *Naphthol blue.* An oxazine derivative obtained by the action of *dimethyl paraphenylene diamine* on *New blue R.* 1889. Dark violet powder, soluble in water with a blue colour. The dry powder is extremely irritating if inhaled. In concentrated H_2SO_4, dirty green solution, which on dilution changes to dirty violet, and then to blue.

Application.—A basic colour. Dyes tannin-mordanted *cotton* blue.

NEW BLUE R (C.) (S.C.I.) (C.R.) (D.) (By.). *New fast blue for cotton* (S.C.I.), *Naphthylene blue R cryst.* (By.), *Fast blue R cryst. for cotton* (Ber.), *Cotton blue R* (B.) (P.), *Fast marine blue* (O.), *Fast cotton blue R, 2 R, 3 R cryst.* (M.), *Fast marine blue*

R M, *M M* (K.), *Phenylene blue*, *Naphthol blue R*, *Meldola's blue*.

Dark violet glistening powder, which is excessively irritating to the mucous membrane. Soluble in water with a violet-blue colour. In concentrated H_2SO_4, dirty green solution, which becomes blue on dilution.

Application.—A basic colour. Dyes tannin-mordanted *cotton* very fast indigo-blue.

NEW COCCIN (Ber.) (M.) *v.* COCHINEAL RED A (B.).

NEW COCCIN R (Ber.) *v.* CRYSTAL SCARLET 6 R (C.).

NEW FAST BLUE F (By.). Brownish powder. Aqueous and alcoholic solution, bright blue. Concentrated H_2SO_4, olive-green solution; on dilution, becomes reddish-blue.

Application.—A basic dye, producing navy blue shades on tannin-mordanted *cotton.*

NEW FAST BLUE H (By.) A similar colour, producing somewhat redder shades.

NEW FAST GREEN 3 B (L.) *v.* VICTORIA GREEN 3 B (B.).

NEW FAST GREY (By.). Black powder. Aqueous and alcoholic solution, reddish-blue. Concentrated H_2SO_4, reddish-blue; on dilution, becomes violet.

Application.—A basic dye. Gives reddish-grey shades on tannin-mordanted *cotton.*

NEW GREEN (M.). A diphenyl naphthyl carbinol derivative. *Dimethyl diamido-naphthyl diphenyl carbinol hydrochloride.* A basic green dye used in *calico* printing.

NEW GREEN (By.) *v.* MALACHITE GREEN.

NEW GREY (By.) *v.* METHYLENE GREY (M.).

NEW MAGENTA (M.). *Iso rubin* (Ber.). A dimethyl derivative of rosaniline hydrochloride (ordinary magenta). *Triamido tritolyl carbinol hydrochloride.* 1889. Green powder, slightly soluble in cold, easily in hot water, with a magenta colour. In concentrated H_2SO_4, yellow solution, which on dilution becomes bright red.

Application.—*v.* MAGENTA. New magenta gives somewhat brighter and bluer colours.

NEW METAMINE BLUE M (L.) *v.* META-MINE BLUE.

NEW METHYLENE BLUE G G (C.). An oxazine derivative obtained by action of *dimethylamine upon New blue R and subsequent oxidation.* 1890. Differs from methylene blue in not containing sulphur. Greenish-grey powder, soluble in water with a blue colour. In concentrated H_2SO_4, reddish-brown solution, which on dilution becomes first green then blue.

Application.—A basic colour. Dyes *wool* or tannin-mordanted *cotton* greenish-blue.

NEW METHYLENE BLUE N (C.). A thiazine derivative. *Diethyl tolu-hionine hydrochloride.* 1891. Metallic-looking crystalline powder, soluble in water with a blue

colour. In concentrated H_2SO_4, yellowish-green solution, which becomes bright blue on dilution.

Application.—A basic colour. Dyes *wool* or tannin-mordanted *cotton* bright blue.

NEW METHYLENE GREY B and G (M.) *v.* METHYLENE GREY.

NEW PATENT BLUE (By.). Similar to PATENT BLUE (*q.v.*).

NEW PHOSPHINE G (C.). An azo dye.

Amidobenzyl dimethylamine — Resorcinol.

1890. Brownish-red powder. Aqueous solution, bright yellow; alcoholic solution, reddish-yellow. Concentrated H_2SO_4, brownish-yellow; on dilution, light yellow.

Application.—A basic colour. Dyes *leather* or tannin-mordanted *cotton*, orange-brown.

NEW PINK *v.* PHLOXIN P.

NEW RED L (K.) *v.* PONCEAU 3 R B (Ber.).

NEW RED (L.). An azo dye.

$$Orthonitrobenzidine \begin{cases} Salicylic\ acid. \\ Alpha\text{-}naphthol\ para\text{-} \\ \qquad sulphonic\ acid. \end{cases}$$

1892. Brownish-red powder, slightly soluble in cold, easily in hot, water, with a red colour. In concentrated H_2SO_4, carmine-red solution, which becomes yellower on dilution.

Application.—A direct cotton colour. Dyes *wool* red from an acid bath; dyes chrome-mordanted *wool* from a neutral bath; dyes *cotton* from a neutral salt bath.

NEW SOLID GREEN B B and 3 B (S.C.I.) *v.* VICTORIA GREEN 3 B (B.).

NEW VICTORIA BLACK B (By.) *v.* VICTORIA BLACK B.

NEW VICTORIA BLACK-BLUE (By.). *v.* VICTORIA BLACK-BLUE.

NEW VICTORIA BLUE R (By.). *Victoria blue R* (B.) (S.C.I.). A diphenyl naphthyl carbinol derivative. *Ethyl tetramethyl tri-amidodiphenyl naphthyl carbinol hydro-chloride.* 1892. Blue powder, somewhat insoluble in water. In concentrated H_2SO_4, brownish-yellow solution, which becomes bright green on dilution.

Application.—A basic colour. Dyes *wool*, *silk*, and tannin-mordanted *cotton*, blue of a redder tone than *Victoria blue B*.

NEW YELLOW (By.) *v.* ORANGE IV.

NEW YELLOW L (K.) *v.* ACID YELLOW (Ber.).

NICKEL, Ni = 59. Nickel occurs as the sulphide in combination with arsenic as *nickel-glance*, NiAsS. The metal has a silver-white colour, and is very hard and takes a fine polish. It is not altered on exposure to the air, and is employed as a coating for iron, &c. (nickel plating), to preserve these substances from rust and the action of acids. It dissolves with difficulty in dilute hydro-

16

chloric and sulphuric acid, but easily in nitric acid. Acetic, tartaric, oxalic, and citric acid have very little effect on nickel unless in contact for a considerable time. Caustic soda when melted in nickel vessels does not attack them. Nickel is a constituent of certain alloys—e.g., German silver, and nickel coins are in use in several countries. Apparatus for laboratory purposes— viz., tongs, spatulas, &c., are often made of nickel.

Nickel Acetate, $Ni(C_2H_3O_2)_2$, is a crystalline salt. When used as a mordant it gives uneven results. The addition of 2 per cent. sodium hydrate causes the immediate fixation of nickel oxide.

Nickel Aceto-Sulphate, $Ni_2SO_4(C_2H_3O)_2$.

C. Gros-Renaud * has recommended this salt (prepared from solutions of nickel sulphate and lead acetate) and the aceto-nitrate for printing. This compound, similarly to the nitrate, sulphocyanide, and nickel ammonium chloride, is difficult to crystallise.

Nickel Aceto-Nitrate, $NiNO_3(C_2H_3O_2)$, is formed by mixing nickel sulphate, lead nitrate, and lead acetate in equivalent proportions.

Nickel Hydroxide, $Ni(OH)_2$, is obtained as an apple-green precipitate, on addition of caustic potash or soda to the solution of a nickel salt; an excess of the precipitant does not re-dissolve the hydroxide. It is slightly soluble in water, and dissolves in ammonia with a blue colour. It is stable in the air, and dissolves readily in sulphuric, nitric, or hydrochloric acid to form nickel salts. An ammoniacal solution of nickel hydrate is used for dissolving silk in the analysis of textile fabrics.

Nickel Sesquioxide, Ni_2O_3, is a black powder, which dissolves in hydrochloric acid with evolution of chlorine and formation of the same chloride as is obtained from the preceding nickel oxide.

Nickel Salts are derived from nickel monoxide, and are prepared by the action of acids on the oxides or on the carbonate. They possess a peculiar apple-green colour; many of them are soluble in water.

Nickel Sulphocyanide, $Ni(CNS)_2$, is prepared from barium sulphocyanide and nickel sulphate. With ammonia it forms a blue solution and deposits crystals. This salt is readily absorbed and fixed by the fibre.

Nickel Sulphate, $NiSO_4 + 7H_2O$, crystallises in green rhombic prisms. It is formed by dissolving nickel or oxide of nickel (NiO) in sulphuric acid.

The double ammonium salt, $(NH_4)_2SO_4$, $NiSO_4 + 6H_2O$, is formed by adding ammonium sulphate to the concentrated acid solution of the preceding compound. It crystallises well. It is used in nickel-plating.

Gros-Renaud fixes nickel salts by treating

* Journ. Soc. Chem. Ind., 1899, p. 367.

the goods with 6 per cent. neutralised Turkey-red oil, drying, and passing through a bath of nickel sulphate, hanging a short time, washing, and dyeing with alizarin colours. Gallein, gallocyanin, and coerulein gave good results, a final soaping producing fast, pure, and brilliant shades.

Liechti and Ulrich * have studied the mordanting properties of various nickel salts on cotton. They succeeded in fixing them either by first impregnating the material with a nickel salt and subsequently passing it through soda, or by first mordanting with Turkey-red oil and subsequently with a nickel salt. Many of the nickel salts crystallise in the fibre and lose their acid very slowly, hence they are little suitable for mordanting. The best results were obtained with the chloride, the nickel-ammonium chloride, the nitrate, the nitrate-acetate, and sulphocyanide; while the sulphate and acetate are less serviceable, owing to their great tendency to crystallise. These authors recommend the nickel-ammonium chloride for dyeing, and the nickel nitrate-acetate for printing, to produce pure colours in light shades. The only use made of the nickel salts in dyeing or printing is for the fixation of the nitroso-colours, such as dinitroso-resorufin, &c.

W. M. Gardner † has studied the behaviour of nickel sulphate and cobalt sulphate as wool mordants. He found that these salts are fixed best without any oxalic acid, tartar, or other acid being added to the mordanting-bath. The salts apparently do not offer advantages over the iron salts, which they resemble in their tinctorial character.

Nickel forms two oxides—the *monoxide* (NiO), and the *sesquioxide* (Ni_2O_3); the former of these gives rise to nickel hydroxide and to the ordinary nickel salts.

NICHOLSON'S BLUE (Br.S.) *v.* ALKALI BLUE.

NIGHT BLUE (B.) (S.C.I.). A diphenyl naphthyl derivative closely allied to *Victoria blue. Tolyl tetra-ethyl triamido diphenyl naphthyl carbinol hydrochloride.* 1883. Violet powder with bronze lustre, soluble in water with a violet-blue colour. In concentrated H_2SO_4, yellowish-brown solution, which on dilution becomes green and then blue.

Application.—A basic colour. Dyes *wool, silk,* or tannin-mordanted *cotton* greenish-blue of very pure tone.

NIGHT GREEN *v.* IODINE GREEN.

NIGRAMINE (Noetzel). Closely allied to *Methylene grey.* Dyes tannin-mordanted *cotton* blue-grey.

NIGRANILINE *v.* ANILINE BLACK.

NIGRISIN (P.) *v.* METHYLENE GREY.

* Journ. Soc. Dyers and Col., 1887, pp. 81, 93.
† Ibid., 1890, p. 39.

NIGROSIN (SOLUBLE IN SPIRIT) v. INDULINE (SOLUBLE IN SPIRIT).

NIGROSIN (SOLUBLE IN WATER) v. INDULINE.

NILE BLUE A (B.) (By.). An oxazine colour. *Diethyl phenyl ammonium amidonaphthoxazine sulphate.* 1888. Bronzy-green crystalline powder, soluble in water. In concentrated H_2SO_4, yellow solution, which becomes green and then blue on dilution.

Application.—A basic colour. Dyes tannin-mordanted *cotton* blue.

NILE BLUE 2 B (B.). Similar to the above. *Diethyl benzyl para-ammonium amidonaphthoxazine chloride.* 1891. Greenish crystalline powder, soluble in water with a greenish-blue colour. In concentrated H_2SO_4, brownish-red solution ; on dilution, violet ppt.

Application.—v. NILE BLUE A.

NILE BLUE R (B.). 1889. A somewhat redder brand.

"NITRATE OF IRON" v. IRON (FERRIC SULPHATE).

NITRATES v. NITRIC ACID.

NITRE v. POTASSIUM NITRATE.

NITRIC ACID, HNO_3, *Aqua fortis.*

Preparation.—Nitric acid is prepared by decomposing sodium nitrate by means of sulphuric acid in cast-iron retorts. The amounts of the ingredients must be such that the following reaction takes place :—

$$NaNO_3 + H_2SO_4 = HNO_3 + NaHSO_4.$$
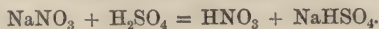
An excess of sulphuric acid is always used so that the normal sodium sulphate (Na_2SO_4) which is difficult to remove from the retorts is not formed. The stills are heated by means of fires placed beneath them. The acid fumes which are evolved are condensed by passing through a series of earthenware jars, the liquid which collects being run into stone bottles from time to time.

Impurities.—The impurities in nitric acid obtained as above are hydrochloric acid, chlorine, sulphuric acid, sodium sulphate, nitrogen peroxide, iodic acid, and iron. In order to remove these impurities the crude acid is distilled in glass retorts, three fractions being taken—1 contains the volatile impurities, viz. :—chlorine, hydrochloric acid, and oxides of nitrogen ; 2 contains nearly pure nitric acid, and forms the bulk of the distillate ; 3, the residue, contains the non-volatile substances mentioned above.

Properties.—Pure nitric acid has a specific gravity of 1·53. It is a colourless liquid, which fumes in the air. On heating to a moderate temperature, the acid turns darker and decomposes to some extent, oxygen and nitrogen tetroxide (N_2O_4) being evolved. At 86° C. the liquid boils and distils. An acid containing 68 per cent. HNO_3, and having a specific gravity of 1·41, distils without de-

composition. Nitric acid has a strong oxidising action ; *fuming nitric acid*, which contains oxides of nitrogen in solution, being very powerful in this respect. This latter substance is prepared by distilling nitric acid with sulphuric acid. Nitric acid can be freed from fumes of oxides of nitrogen by blowing air through.

Most organic substances are more or less attacked by nitric acid ; many substances—*e.g.*, sawdust, straw, &c.—ignite when thus treated ; turpentine and alcohol explode in

SPECIFIC GRAVITY OF NITRIC ACID AT 15° C., COMPARED WITH WATER OF 4° C., AND REDUCED TO VACUUM (*Lunge and Rey.*)

Degrees Twaddel.	Per cent. HNO_3 by Weight.	Degrees Twaddel.	Per cent. HNO_3 by Weight.
0	0·10	53	42·10
1	1·00	54	42·87
2	1·90	55	43·64
3	2·80	56	44·41
4	3·70	57	45·18
5	4·60	58	45·95
6	5·50	59	46·72
7	6·38	60	47·49
8	7·26	61	48·26
9	8·13	62	49·07
10	8·99	63	49·89
11	9·84	64	50·71
12	10·68	65	51·53
13	11·51	66	52·37
14	12·33	67	53·22
15	13·15	68	54·07
16	13·95	69	54·93
17	14·74	70	55·79
18	15·33	71	56·66
19	16·32	72	57·57
20	17·11	73	58·48
21	17·89	74	59·39
22	18·67	75	60·30
23	19·45	76	61·27
24	20·23	77	62·24
25	21·00	78	63·23
26	21·77	79	64·25
27	22·54	80	65·30
28	23·31	81	66·40
29	24·08	82	67·50
30	24·84	83	68·63
31	25·60	84	69·80
32	26·36	85	70·98
33	27·12	86	72·17
34	27·88	87	73·39
35	28·63	88	74·68
36	29·38	89	75·98
37	30·13	90	77·28
38	30·88	91	78·60
39	31·62	92	79·98
40	32·36	93	81·42
41	33·09	94	82·90
42	33·82	95	84·45
43	34·55	96	86·05
44	35·28	97	87·70
45	36·03	98	89·60
46	36·78	99	91·60
47	37·53	100	94·09
48	38·29	101	96·39
49	39·05	102	98·10
50	39·82	103	99·07
51	40·58	104	99·67
52	41·34		

contact with the acid. The concentrated acid when dropped on the skin causes deep wounds, which heal very slowly. Many substances turn yellow in contact with the acid; wool, silk, and feathers are thus affected. Nitric acid dissolves all metals except gold and platinum, producing salts, called *nitrates*, and evolving oxides of nitrogen. Very dilute solutions of nitric acid are reduced by metals to ammonia, no gases being given off.

Many non-metals, as, for example, carbon, phosphorus, and sulphur, are oxidised by nitric acid, the corresponding acids being formed. Indigo solution is decolourised by nitric acid. Commercial nitric acid is yellow in colour, owing to the presence of lower oxides of nitrogen, the impurities mentioned above being also present. Its specific gravity is 1·35 to 1·44, and it is frequently known as *aqua fortis.*

Fuming nitric acid is prepared by distilling aqua fortis with excess of sulphuric acid. It is a red-brown liquid containing oxides of nitrogen, and is a very powerful oxidising agent.

Uses.—Nitric acid is extensively employed for many purposes, viz. :—in the manufacture of sulphuric acid, coal-tar colours, nitroglycerin, in the preparation of certain mordants, &c.

AQUA FORTIS is impure nitric acid which contains a considerable amount of the lower oxides of nitrogen. The ordinary commercial nitric acid is also frequently called aqua fortis.

The strength of nitric acid is determined by acidimetric titration, or by the hydrometer (see table, p. 243).

NITRO-HYDROCHLORIC ACID *v.* AQUA REGIA.

NITRO-MURIATE OF TIN *v.* TIN SPIRITS.

NITROPHENINE (Clayton Aniline Co.). An azo dye.

　　　　Paranitraniline — Primuline.

1893. Brown powder, giving a reddish-yellow solution in water. In concentrated H_2SO_4, golden yellow solution; on dilution, yellow ppt.

Application.—A direct cotton colour. Dyes *cotton* yellow from an alkaline salt bath.

NITROSAMINE RED (B.). An *azotised paranitraniline.* *v.* AZO COLOURS ON COTTON.

NON-MORDANT COTTON BLUE (Br.S.) *v.* ALKALI BLUE X G (Br.S.).

NOPALIN *v.* EOSIN B N.

NORMAL SOLUTIONS *v.* ACIDIMETRY.

NYANZA BLACK B (Ber.). A primary azo dye.

Alpha-naphthyl- ⎰*Phenylene diamine.*
amine ⎱*Amidonaphthol gamma-*
　　　　　　　sulphonic acid.

1892. Black powder, insoluble in cold water. Alcoholic solution, reddish-blue. Concentrated H_2SO_4, bright blue; on dilution becomes violet.

Application.—A direct cotton colour. Specially suitable for wool dyeing.

O

OAK GALL NUTS *v.* GALL NUTS.
OENANTHININ (D. & H.) *v.* AMARANTH.
OIL OF VITRIOL *v.* SULPHURIC ACID.
OILS *v.* LUBRICATING OILS.
OILS (WOOL) *v.* OLIVE OIL.
OLD FUSTIC *v.* FUSTIC (OLD).
OLEATES *v.* OLIVE OIL.
OLEIC ACID, $C_{17}H_{33}$(COOH).

Preparation.—Pure oleic acid can be prepared by saponifying olive oil with alkali. The soap which is formed is decomposed with dilute acid, and the mixture of fatty acids digested with litharge at a moderate temperature. Lead oleate is soluble in ether, hence it can be extracted by that solvent. The etherial solution of lead oleate is acidified with hydrochloric acid, washed free from lead by means of water, and the ether driven off from the oleic acid at a low temperature.

Properties. — Oleic acid when pure is a colourless oil, which solidifies to a white mass at 4° C. It is decomposed on heating alone, but is volatile in steam. It is insoluble in water, but dissolves in alcohol and in ether.

Oleic acid is monobasic and forms salts called *oleates* (the salts of the alkalies are soaps), which are similar to the stearates and palmitates. The pure acid is not altered on exposure to the air; the commercial acid turns yellow and becomes rancid.

Oleic acid can be converted into stearic acid by means of nascent hydrogen,

$$C_{18}H_{34}O_2 + H_2 = C_{18}H_{36}O_2.$$

Concentrated sulphuric acid dissolves oleic acid, the product being *sulpholeic acid*, the ammonium or potassium salt of which is called *Turkey-red oil.*

Oleic acid absorbs bromine, forming dibrom stearic acid,

$$C_{18}H_{34}O_2 + 2Br = C_{18}H_{34}Br_2O_2.$$
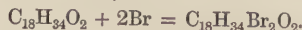
Nitrous acid converts oleic acid into the isomeric *elaidic acid*, which melts at 45° C. Commercial oleic acid is known as *red oil.*

Commercial Oleic Acid, Oleine, Red Oil,[*] is obtained by subjecting to hydraulic pressure the mixture of fatty acids produced by the saponification of tallow, palm oil, and similar fats. The expressed liquid technically known as "red oil" contains a con-

---

[*] A. H. Allen, *Com. Org. Analysis*, vol. ii., pt. 1.

siderable quantity of palmitic and stearic acids, which separate out on keeping the red oil at a low temperature for some time.

"Oleine," as commercial oleic acid is frequently improperly called, is sometimes a clear liquid ranging in colour from dark brown to pale sherry, while other specimens are quite pasty owing to the presence of solid fatty acids. The specific gravity ranges from ·897 to ·905.

Analysis.—*Mineral acids* are sometimes present in sensible quantity. They rarely interfere with its applications, but may be detected and estimated by agitating the sample with hot water and examining the aqueous liquid.

The presence of an abnormal proportion of *oxidation* and *secondary products* of an acid character is indicated by agitating 50 c.c. of the oleic acid with 1 c.c. of a 10 per cent. solution of ammonia and 50 c.c. of water. Both the oleic acid and the aqueous liquid should by this means be deprived of any acid reaction to litmus.

The presence of *palmitic* or *stearic acid* may be detected by saponifying the sample with alcoholic potash, adding a drop of phenolphthaleïn solution and then acetic acid drop by drop until the pink colour is destroyed. The liquid is then filtered, mixed with twice its weight of ether, and an alcoholic solution of lead acetate added. Any white precipitate may consist of stearate or palmitate of lead, which may be filtered off, washed with ether, decomposed with dilute hydrochloric acid, and the liberated fatty acids weighed. All ordinary commercial oleic acid will indicate the presence of foreign fatty acids when examined in this way.

Neutral oils or glycerides will be indicated by the separation of oily drops, if equal measures of the sample and of alcohol are heated to 25° C. for some time, while a pure acid will give a clear solution when thus treated. A very delicate test for neutral oils in oleic acid, consists in dissolving the sample in hot alcohol, and adding a few drops of strong ammonia, when mere traces of glycerides will cause a strong turbidity.

The presence of *fixed oils* or *hydrocarbon oil* can also be inferred from the proportion of alkali required, when the sample is titrated in alcoholic solution, using phenolphthaleïn as an indicator. Five grms. of pure oleic acid will require 35·47 c.c. of semi-normal caustic alkali, corresponding to 19·9 per cent. of KOH, and a combining weight of 282. Hence the percentage of *oleic acid* in the sample may be found by dividing the percentage of KOH required by 0·199. Any admixture of palmitic acid will *increase* the amount of alkali required.

The neutralised liquid from the last process may be heated on a reversed condenser for half an hour, and then the excess of alkali remaining, titrated with semi-normal hydrochloric acid until the red colour disappears (Koettstorfer's saponification process), when each 1 c.c. of additional semi-normal alkali used in saponifying the neutral oil will indicate the presence of 0·145 grm. of *neutral fixed oil* in the sample. The liquid left after the second titration may be evaporated with a further quantity of alcoholic potash, the residual soap dissolved in water, and the solution agitated with ether. The etherial solution is then separated, the alkaline liquid re-extracted with ether, and the etherial solutions, after mixing, agitated with water, separated, evaporated, and the residual *unsaponifiable matter* weighed.

In the case of an oleic acid obtained by the distillation of an ordinary fat with super-heated steam, the unsaponifiable matter or ether-residue obtained in the last process consists of *hydrocarbons* presenting the closest resemblance to those obtained in the lubricating oils manufactured from petroleum and bituminous shale. Hence no means exist at present by which an intentional addition of a moderate proportion of hydrocarbon oil to oleic acid can be positively detected. The hydrocarbons normally present in distilled oleic acid range from 3 to 7 per cent., and therefore any proportion notably in excess of the latter figure may be attributed to an intentional sophistication of the product with mineral or shale oil. The addition of these adulterants to oleic acid is extensively practised, although their presence greatly reduces the suitability of the oleic acid for greasing wool during the process of spinning. Any admixture of hydrocarbon oil reduces the property of ready saponifiability, for which the oleic acid is chiefly valued.

Wool grease and the grease obtained by treating with acid the soapy liquors in which wool has been washed are much more impure articles. Besides the *hydrocarbons* formed on distilling such greases, the distilled product is liable to contain *actual* petroleum or shale products, used in the wool spinning, either intentionally or as adulterants of other oils, petroleum employed for antiseptic purposes on the living sheep, and *cholesterin* and other unsaponifiable substances contained in the "suint," or wool fat. Hence, an estimation of the "unsaponifiable matter" in such low-class oleic acids cannot be regarded as a reliable indication of the extent to which they have been adulterated by an actual addition of hydrocarbon oil. Some indication of the origin of the unsaponifiable matter may be obtained by treating it with thrice its volume of rectified spirit, when the amount left undissolved may be regarded as indicating roughly the amount of hydrocarbon oils present, while the cholesterin and any

solid alcohols derived from sperm or bottle-nose whale oil will pass into solution.

Adulteration of Commercial Oleic Acid with Linoleic Acid and its Drawbacks.[*]—Oleic acid used for greasing wool preparatory to spinning is, if adulterated with the fatty acids from linseed oil, liable to cause yellow stripes on the finished fabric, which are not removable by sulphur stoving, and are visible even after dyeing in light coloured goods. The thread itself appears rough and sticky, there is an increase in waste, and scouring becomes difficult. In the manufacture of candles, linseed oil, owing to the percentage of solid fatty acid it yields, increases the weight of candle material, whilst the liquid portions remain mixed with the oleic acid of tallow.

Oleic and *linoleic acid* in mixtures may be distinguished as follows :—

Linoleic acid is lighter coloured than commercial oleic acid ; its specific gravity is 0·912 to 0·919 against 0·965. A mixture of the two acids heated to 50° C. stiffens on cooling ; by repeated heating and cooling the consistency of butter is reached.

A thin layer of oleic acid on a piece of sheet-lead remains almost unchanged for a day ; admixture of linoleic acid makes it dry more or less.

Shaken with an equal volume of caustic soda, a mixture turns intensely yellow ; pure oleic acid becomes grey.

Impure oleic acid, on treatment with Poutets' reagent (mercury or so-called elaidin tests), will be found more or less soft after twenty-four hours, according to the percentage of linoleic acid present ; pure oleic acid becomes entirely solid. *v.* OLIVE OIL (ANALYSIS OF).

Linseed oil is detected in commercial oleic by Hazura[†] as follows :—50 grms. of the sample are saponified on the water-bath with dilute alcoholic potash. After evaporation of the alcohol, the residual soap is dissolved in 1 litre of water. One litre of 5 per cent. solution of potassium permanganate is then gradually added to the soap solution with constant shaking. In about an hour the hydrated manganese peroxide is filtered off, the filtrate acidified with sulphuric acid and again filtered. The filtrate is next neutralised with caustic potash, concentrated to about 300 c.c., and again acidified with sulphuric acid, a precipitate being thus obtained. The acid solution, containing the precipitate, is then agitated with ether.

If the precipitate dissolve in ether, it consisted of pure azelaic acid, $C_9H_{14}O_4$, and the sample of oleine is free from linseed oil acids ; but if the precipitate does not dissolve in ether, this may be owing to the presence of these acids. The precipitate is filtered, re-crystallised several times from alcohol or water, and decolorised by animal charcoal. After drying in a desiccator, its melting point is determined. If the latter be above 160° C., linseed oil acids are present.

OLEINE *v.* OLEIC ACID (COMMERCIAL).

OLEIN, TRIOLEIN, $(C_{18}H_{33}O_2)_3C_3H_5$. This substance, which is the glyceride of oleic acid, is the true oleïn. It is the principal constituent of olive oil, and is present in most non-drying oils, such as cod-liver oil, lard, tallow, palm oil, &c.

The majority of animal and vegetable fats and oils consist of the glycerides of oleic, palmitic, and stearic acids. The two latter (palmitin and stearin) are solid, olein is a liquid at temperatures above 6° C. As a rule, the fluidity of a fat or oil of the above-mentioned kinds depends on the percentage of olein present.

Olein, like the other glycerides, undergoes decomposition on distilling, *acrolein* (C_3H_4O)—which has the characteristic smell of burning fat—being formed. On exposure to air olein commences to decompose, becoming "rancid." The same reaction is completed when olein is heated with dilute acids, alkalies, or lime, or even by the action of steam, free oleic acid and glycerin being formed. This process is termed "saponification." The sodium and potassium salts of the liberated acid are termed "soaps." Lead oxide also forms a soap called "lead plaster." The lead plasters are used as mordants for the eosins, &c. The fibre is first treated with soap solution, and then passed through a solution of a lead salt.

OLIVE OIL is extracted from the ripe fruit of the olive tree, which flourishes in Southern Europe.

Preparation.—The oil obtained by grinding and pressing the olives is the best quality, and is largely used as an article of diet. The residual mass, termed *marc*, yields, on treating with hot water and applying pressure, a second quality of oil, which is of a yellow colour. Carbon bisulphide is employed to extract the remaining oil from the pasty residue. This is an inferior product, having a brownish- or greenish-yellow colour and possessing an unpleasant odour.

Properties.—The specific gravity of olive oil fluctuates between 0·914 and 0·917 at 15° C., but that of hot-pressed oil, in which the amount of palmitin and stearin is large, may rise to 0·925.

Olive oil consists of about 72 per cent. olein (the triglyceride of oleic acid), the remainder being palmitin and stearin. The two latter substances are deposited almost completely at 0° C., and may then be separated from the olein by pressure. Olive oil does not dry on exposure to the air, but gradually becomes rancid, oleic acid being liberated.

---

* Granval and Valser, *Chem. Zeit.*, vol. xiii., p. 23.
† *Journ. Soc. Chem. Ind.*, 1889, p. 641.

If the oil be boiled with acids or treated with steam, the same reaction takes place.

$$C_3H_5(C_{18}H_{33}O_2)_3 + 3H_2O$$
Olein.

$$= C_3H_5(OH)_3 + 3C_{18}H_{34}O_2.$$
Glycerin.   Oleic acid.
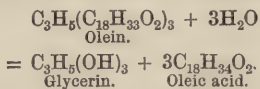
On shaking olive oil with dilute sodium carbonate solution an emulsion is formed. On standing, this separates into two layers, the upper stratum consisting chiefly of oil. The presence of fatty acids in the olive oil causes the formation of " soap," which assists in making the emulsion more permanent. In this emulsion the glycerides, olein, palmitin, and stearin, which do not unite with alkalies in the cold, exist in a finely divided state, in which form the oil is easily absorbed by the cotton fibre.

Gallipoli oil (huile tournante) is a variety of olive oil containing much free acid, having become rancid. It is particularly adapted for the production of emulsions, which are used in the dyeing of Turkey-red.

Uses.—In *calico* printing, olive oil is used as an admixture to the printing colour with the object of making the paste smooth and free from air bubbles.

Olive oil is employed as a lubricant, for oiling wool, in the preparation of sulphated oil, and for softening silk after dyeing.

The Influence of Olive Oil used in Oiling Wool on the Subsequent Dyeing Operations. [*]

Although the oiling of wool necessary before carding is merely a preliminary operation to spinning, it is nevertheless of great importance to the dyer, in so far as a proper selection of the material serving for oiling is essential to the production of an even shade. An admixture of *resinous oils, mineral oils,* and *drying oils* to the oiling substances create disturbances in the dyeing process, although the action of these substances has not yet been scientifically explained. In practice their presence renders the production, especially of light shades, much more difficult, and is generally considered as one of the causes of unevenness. The resinous oils and the mineral oils being unsaponifiable ingredients of the oiling substance, are certainly injurious, because they cannot be removed from the woollen fibre by the treatment usual in the manufacture, and in the subsequent dyeing process they are obstructive to an even penetration of the colouring matter into the wool fibre. But this effect being probably produced by all other unsaponifiable fats, the condition made hitherto that the oils are to contain no resinous or mineral oils may be

* A. Horwitz, *Journ. Soc. Dyers and Col.*, 1890, p. 126.

extended so far that they are to be free from any unsaponifiable ingredients. An unsaponifiable fat, frequently found in the oiling substances, is cholesterin ($C_{26}H_{44}O + H_2O$), a sticky matter which easily crystallises. The presence of cholesterin is more obstructive to an even fixation of the colouring matter than that of any other unsaponifiable ingredient, consequently all oils to be used for wool should be tested for cholesterin. The detrimental effect of the drying oil may be caused by the wool fibre being enveloped by a coat of varnish, which would partly prevent the entrance of the colouring matter.

A pure olive oil is obtained by pressing the olives in the cold ; the second yield, obtained by boiling the olives and by hot pressure, is the product which is chiefly used for oiling wool. It consists chiefly of triolein (about 72 per cent.), and contains besides palmitin, arachin, arachinic acid, and very little stearin.

With the usual methods of preparing the oil, the quantity of cholesterin passing into the olive oil will be very small, so that the presence of such traces will scarcely have a perceptible influence. But if the amount of cholesterin in an oil should be about 4 per cent., as has frequently been observed, the oil is of the poorest quality and has been obtained by unusual ways of preparation. In one instance cholesterin having been extracted from dyed pieces that were spotted, the olive oil used in oiling the wool was found to contain 3 per cent. of cholesterin.

The olive oils of commerce are extensively adulterated with less expensive oils. An addition of non-drying vegetable oils can only interest the spinner, while in dyeing it can scarcely have any bad effect. An admixture of drying oils, resinous or mineral oils, will, on the contrary, create more or less conspicuous disturbances in dyeing. These adulterations will be detected by the chemist by a change in the iodine and saponification equivalents, as well as by deviations in the melting and solidifying points of the fatty acids.

The presence of *drying oil* may be shown qualitatively, as follows : — A well-cleaned copper wire is placed in a mixture of 2 c.c. of nitric acid and 5 c.c. of oil ; the mixture is then stirred with a glass rod. If the sample contained a drying oil, the wire if withdrawn after half an hour will have a pink shade.

The test for *resinous* or *mineral oil* requires the oil to be saponified, the dried soap to be extracted with petroleum ether, and a further examination of the residue after evaporation of the ether. According to Allen, a mixture of 10 drops of resinous oil with bromide of tin is coloured a brilliant

purple. Bromide of tin may be prepared by adding bromine, after having shaken it with sulphuric acid, for the purpose of taking the water from it, drop by drop, on tin filings kept in a well-cooled bottle.

For *cholesterin* the unsaponifiable portion may be tested by the following reactions proposed by Schulze :—

1. If a small quantity of cholesterin is carefully evaporated to dryness with a few drops of nitric acid on the lid of a crucible, a yellow spot remains, which, if ammonia be poured on it, assumes a yellowish-red colour.

2. If a sample of cholesterin is rubbed on the lid of a crucible, with a drop of a mixture of three volumes of concentrated sulphuric acid and one volume of solution of ferric chloride, then carefully evaporated to dryness, the undissolved particles assume a violet-red colour, which gradually turns more towards blue.

3. If a sample of cholesterin is rubbed together with a little concentrated sulphuric acid, and chloroform is then added, a blood-red solution is produced, which on the admixture of concentrated nitric acid becomes violet-blue, then colourless.

If an olive oil destined for oiling wool contains several of these damaging admixtures at the same time, it becomes a matter of great difficulty to answer the question so frequently put in practice as to what extent the oil may have an injurious influence in the further course of the manufacturing operation. Researches in which the quantity of the admixed substances, as well as the amount of damage caused by them, are taken into account, have not yet been made, so that even a calculation of probability, which alone might lead to a result, is as yet impossible.

Lastly, there is another point which is not, indeed, of immediate interest to the dyer, but in other respects of paramount importance—namely, that all oiling materials for wool should not contain any free acid, which strongly attacks the cards, destroying them in a short time.

Analysis.—In deciding as to the genuineness or otherwise of a sample of olive oil, the following determinations are necessary :— The specific gravity at 15° C., the amount of unsaponifiable matter, Maumené's test, the elaidin test, the saponification equivalent, the melting point of the fatty acids and their mean molecular weight and iodine number : the iodine absorption number of the oil is also useful. In many cases special tests must be applied, as mentioned above.

Maumené's Test. — 50 grms. of oil are weighed off in a beaker, and 10 c.c. of concentrated sulphuric acid at the same temperature added. The mixture is stirred by means of a thermometer until no further rise of temperature takes place. The difference between the original and the last thermometer readings is the Maumené number. As olive oil gives a smaller increase of temperature when thus treated than any oil which might be used to adulterate it, any rise of temperature exceeding 44° C. will point to probable adulteration.

The Elaidin Test.—2 c.c. of a freshly-prepared solution (made by acting on 1 c.c. of mercury with 12 c.c. of cold nitric acid of 1·42 specific gravity) are added to 50 c.c. of the olive oil, and the mixture thoroughly shaken in a bottle. The bottle is placed in a vessel containing water (in order to keep the temperature constant), and shaken every five minutes during two hours. The temperature of the water should be from 15° to 20° C. In less than two hours a pure olive oil thus treated will be converted into a hard pale yellow mass. The presence of other oils is indicated by the orange or red colour, and the softness of the elaidin.

Unsaponifiable Matter v. OILS — LUBRICATING.

Melting Point and Mean Molecular Weight of Fatty Acids v. SOAP ANALYSIS.

Free Fatty Acid may be estimated as in *Lubricating oils* (q.v.).

The iodine value is determined as follows (Hübl's test) :—0·2 grm. of the oil or fatty acid is carefully weighed off and transferred to a stoppered bottle of 600 c.c. capacity, 10 c.c. of chloroform are added, and 25 c.c. of the iodine solution (prepared as below) are run in from a burette. The bottle should be kept in the dark for six hours. It should be examined after standing for some time, and if the brown colour has disappeared, 25 c.c. more iodine solution must be added. A blank experiment must be simultaneously carried out in a precisely similar manner without oil. At the end of the time mentioned 15 c.c. of 10 per cent. potassium iodide solution and 50 c.c. water are added to the contents of the bottles, and $\frac{N}{10}$ sodium thiosulphate run in with constant stirring from a burette. When the colour of the solution is a pale yellow, starch paste is added and the titration continued until the blue colour is just discharged.

Preparation of the Iodine Solution.—30 grms. of mercuric chloride are dissolved in 500 c.c. of pure 95 per cent. alcohol. The filtered liquid is kept in a stoppered bottle. 25 grms. of iodine are also dissolved in half a litre of pure alcohol, and the liquid kept in the dark.

When the solution is required, equal volumes of the two solutions are mixed and allowed to stand one hour in the dark before adding to the fat.

Example.—Oil taken, 0·2171 grm.

Blank test required 25·12 c.c. hyposulphite.
Experiment ,, 10·75 c.c. ,,

———

14·37 c.c. ,,

Grms. Iodine.

1 c.c. $\frac{N}{10}$ hyposulphite = 0·0127

∴ 14·37 c.c. ,, = 0·0127 × 14·37

∴ $\frac{0·0127 \times 14·37 \times 100}{0·2171}$ = 84·24 % iodine.

The iodine value of olive oil ranges from 81·5 to 84·5. A higher number than 85 is suspicious, although in some particular kinds of oil (Californian and Colombaic) 88 is sometimes found.

Cottonseed oil is detected by adding to the oil an equal quantity of nitric acid of 1·37 specific gravity, and shaking vigorously. If cottonseed oil be present a brown coloration will be produced on standing, which varies in intensity with the amount of the adulterant.

OPAL BLUE (C.) (Br. S.) *v.* GENTIANA BLUE 6 B (Ber.).

OPAL BLUE (C.) *v.* SOLUBLE BLUE.

ORANGE I (many makers). *Naphthol orange* (Ber.), *Orange B* (L.), *Alpha-naphthol orange, Tropaeolin O O O No. 1.* An azo dye.

Sulphanilic acid — Alpha-naphthol.

1876. Reddish - brown powder, soluble in water, with an orange-red colour. In concentrated H_2SO_4, violet-red solution, which becomes reddish-brown on dilution.

Application.—An acid colour. Dyes *wool* and *silk* orange from an acid bath.

ORANGE II (many makers). *Orange P* (O.), *Orange extra* (C.), *Orange A* (L.), *Acid orange* (G.), *Atlas orange* (Br. S.), *Gold orange* (By.) (D.), *Mandarin G extra* (Ber.), *Beta-naphthol orange, Tropaeolin O O O No. 2.* An azo dye.

Sulphanilic acid — Beta-naphthol.

1876. Yellowish - red powder, soluble in water. In concentrated H_2SO_4, magenta-red solution ; on dilution, brownish-red ppt.

Application.—An acid colour. Dyes *wool* or *silk* orange from an acid bath.

ORANGE III (many makers). *Helianthine* (B.), *Dimethylaniline orange, Methyl orange, Gold orange, Tropaeoline D.* An azo dye.

Sulphanilic acid — Dimethylaniline.

1875. Ochre-yellow powder, giving an orange-yellow solution in water. In concentrated H_2SO_4, brown solution, which becomes magenta-red on dilution.

Application.—An acid colour. Dyes *wool* and *silk* orange from an acid bath. Used in volumetric analysis as an indicator under the name *Methyl orange.* Its aqueous solution is reddened by acids (excepting carbonic acid).

ORANGE IV (many makers). *Orange N* (B.) (S.C.I.), *Orange M* (L.), *Orange G S* (O.), *New yellow* (By.), *Acid yellow D* (Ber.), *Helioxanthine, Fast yellow* (Br. S.), *Diphenylamine orange, Diphenyl orange, Tropaeolin O O* (C.). An azo dye.

Sulphanilic acid — Diphenylamine.

1876. Orange - yellow plates or powder, soluble in water. In concentrated H_2SO_4, violet solution, which gives a violet ppt. on dilution.

Application.—An acid colour. Dyes *wool* and *silk* orange-yellow from an acid bath. Fast to light.

ORANGE A (L.) *v.* ORANGE II.

ORANGE B (L.) *v.* ORANGE I.

ORANGE ENL (C.) *v.* CROCEINE ORANGE.

ORANGE EXTRA (C.) *v.* ORANGE II.

ORANGE G (Ber.) (B.) (M.). *Orange G G* (C.) (D.), *Patent orange* (Ber.). An azo dye.

Aniline — Beta-naphthol gamma-disulphonic acid.

1878. Yellowish - red powder, giving an orange-red solution in water. In concentrated H_2SO_4, orange-yellow solution ; unchanged on dilution.

Application.—An acid colour. Dyes *wool* orange-yellow from an acid bath. The colour is very fast to light.

ORANGE G G *v.* ORANGE G.

ORANGE G R X *v.* CROCEINE ORANGE.

ORANGE G S (O.) *v.* ORANGE IV.

ORANGE G T (By.). *Orange R N* (C.), *Brilliant orange O* (M.), *Orange N* (K.). An azo dye.

Toluidine — Beta-naphthol sulphonic acid S.

1879. Scarlet powder, giving an orange-red solution in water. In concentrated H_2SO_4, red solution, from which brown oily drops separate on dilution.

Application.—An acid colour. Dyes *wool* orange-yellow from an acid bath.

ORANGE M (L.) *v.* ORANGE IV.

ORANGE M N (S.C.I.) *v.* METANIL YELLOW (O.).

ORANGE N (B.) *v.* ORANGE IV.

ORANGE N (K.) *v.* ORANGE G T (By.).

ORANGE N (K.) *v.* BRILLIANT ORANGE R (M.).

ORANGE O P (O.) *v.* ORANGE II.

ORANGE R (C.) (D. & H.) (S. C. I.) *v.* ORANGE T (K.).

ORANGE R (B.). *Orange R R* (S.C.I.). An azo dye.

Xylidine sulphonic acid — Beta-naphthol.

1875. Bright red powder, soluble in water with an orange colour. In concentrated H_2SO_4, cherry - red solution ; on dilution, brown ppt.

Application.—An acid colour. Dyes *wool* or *silk* reddish-orange from an acid bath.

ORANGE R (Sandoz) *v.* ALIZARIN YEL-
LOW R (By.).

ORANGE R L and R R L (C.). Identical
with, or very similar to, RESORCIN YELLOW.

ORANGE R N (C.) *v.* ORANGE G T (By.).

ORANGE R R (S.C.I.) *v.* ORANGE R (B.).

ORANGE T (K.). *Orange R* (D. & H.)
(S. C. I.), *Mandarin G R* (Ber.), *Kermesin
orange* (L.). An azo colour.

*Orthotoluidine mono-
sulphonic acid* — *Beta-naphthol.*

1886. Brick-red powder, giving an orange
solution in water. In concentrated H_2SO_4,
magenta-red solution; on dilution, yellowish-
brown.

Application.—An acid colour. Dyes *wool*
or *silk* orange from an acid bath.

ORANGE T A (Ber.) (By.). Light red
powder. Aqueous solution, orange-yellow;
alcoholic solution, orange. Concentrated
H_2SO_4, bright blue; on dilution, blue ppt.

Application.—A direct cotton colour. Gives
bright reddish-orange shades on unmordanted
cotton.

ORCEIN *v.* ORCHIL (CHEMISTRY OF).

ORCELLIN No. 4 *v.* FAST RED A (B.).

ORCHIL and CUDBEAR. Purple dyes
derived from certain lichens, and correspond-
ing to the dye we now know as orchil, were
certainly in use before the Christian era;
but the art of producing the dye appears to
have been entirely lost for many centuries,
and was re-discovered by a Florentine named
Frederigo, about the year 1295.

An alternative source of supply of the raw
material was found in the Canaries about
the year 1410, and the method of manufac-
ture becoming known, the Italian monopoly
was quickly lost. At a considerably later
date (1730-40) the orchil-producing lichens
were found in great abundance in the Cape
de Verde Islands, and they are still imported
from the above-mentioned sources, as well as
from Zanzibar, Madagascar, California, &c.
Some varieties of the lichens may be found
in almost every district, in quantities which
are, however, insufficient to form regular
sources of supply.

Origin. — The *lichens* are small cellular
perennial plants, forming a distinct class of
Cryptogamia, intermediate between the *algæ*
and *fungi*. Varieties grow in all climates.
Some species flourish in tropical countries,
while the vegetation of Arctic regions consists
mainly of lichens and algæ. The economic
uses of these plants are very varied, some
species being edible, others being of value
medicinally, while many yield purple, yellow,
or brown dyes under suitable treatment.

As a source of colouring matter, only those
species are commercially important which
produce a purple dye; but many others are
used in certain localities as yellow and brown

dyes, of which the following may be men-
tioned: — *Raminalia scopulorum, Parmelia
saxatilis, P. omphaloides, Rembilicana scru-
posa,* and several species of *Physcia.*

The lichens which are employed in the
manufacture of orchil are various species of
Roccella, Lecanora, and *Variolaria.* Their
appearance and habitat are extremely varied,
some growing upon the bark of trees, others
upon rocks, whilst other varieties thrive on
earth or sandy soil.

The following are the chief varieties com-
mercially used in making orchil in this
country:—

(1) *Roccella tinctoria,* which grows upon
rocks near the sea coast in the form of a
bushy group of branches a few inches long,
springing from a round stem. The bran-
ches may be round or flat, and are very
strong and wiry. They usually subdivide,
and end in sharp, horny points. In colour
the weed varies from pale grey to pale brown,
and this is the variety which was used by
the old Florentine manufacturers. It is now
imported from Madeira, the Canary and Cape
de Verde Islands, East Indies, Madagascar,
Zanzibar, Senegambia, Cape Horn, and South
and Central America. In small quantities it
is also found on the south coast of England.
The quality (orchil-yielding capacity) of the
weed varies considerably in samples from
different localities. Thus, the commercial
varieties distinguished as "Angola" weed,
"Canary," "Valparaiso," and "Cape Verde,"
are all from *Roccella tinctoria,* but the market
price of "Angola" is about double that of
"Cape Verde."

(2) *Roccella fuciformis* is a fine, bunchy,
flat-leaved lichen, white in colour, imported
in large quantities from the west coast of
Africa and from California, and is sold as
"Californian" or "Lima" weed. It is some-
what less esteemed than a good quality of *R.
tinctoria.*

(3) *Roccella montagnei* has much broader
leaves than *R. fuciformis,* but is otherwise
similar in appearance. It is exported from
Ceylon, Madagascar, and the east coast of
Africa, and is considered a good quality of
weed.

(4) *Lecanora tartarea,* an inland weed,
grows in Sweden and Norway. It is also
found in the north of Scotland and rarely in
England, but specimens have been met with
in Yorkshire. The *L. tartarea* differs much
from the *Roccellæ* in appearance, forming
upon the rocks on which it grows, white flat
crustaceous masses, with brown fissures of
irregular shape.

(5) *Variolaria dealbata* and

(6) *V. orcina* are also found on rocks, the
former in the Alps and Pyrenees, and the
latter in Auvergne.

(7) *Usnea florida* possesses green fibrous

leaves, each containing a yellow nodule surrounded by small radiating branchettes. It grows upon the bark of trees in tropical countries, and is one of the less important of the orchil-producing lichens.

(8) *Cladonia rangiferina* is a white and woody ground lichen, which grows taller than most species.

The total amount of lichens used for the production of orchil is very considerable, the annual amount converted into colouring matter in this country alone being upwards of 2000 tons.

MANUFACTURE OF ORCHIL.

The lichens do not contain any ready formed colouring matter, the latter being produced by the action of ammonia and oxygen upon the crushed weeds. The process of manufacture is somewhat as follows :—The lichen is torn, cut or ground into small pieces, and placed in a large horizontal boiler, fitted with a steam pipe for heating, and a mechanical stirrer. Some manufacturers then extract the weed with water at a temperature of about 50° C., but a more usual plan is to add at once about 4 per cent. of the weight of weed of strong ammonia (0·88 sp. gr.). The amount of water used is just sufficient to cover the weed. After closing the boiler, the mass is heated for about six hours at a temperature of 25° to 30° C., stirring at intervals, and is then allowed to stand for two days, after which the fermentation will be well established. Another 4 per cent. of ammonia is now added, and the mass stirred three times daily, and exposed to the air at suitable intervals, the temperature being maintained at 25° to 30° throughout. A further small addition of ammonia may be necessary in order to fully develop the colour, the process lasting altogether for from fifteen to twenty days. Over-fermentation results in the destruction of the colouring matter, the purple being changed to brown.

At the end of the operation some manufacturers add milk of lime and carbonate of soda, others use sodium carbonate along with the ammonia, in the first instance, and claim better results. Ammonia cannot, however, be replaced by other alkalies, since it has a specific action, as is explained below.

The particular shade of orchil produced depends principally upon the character and amount of alkali present. The red shade is usually produced by heating the paste at a low temperature to drive off the ammonia, but may be also formed by adding a small amount of red prussiate of potash solution to the blue orchil extract.

The most recent improvement in the manufacture of orchil consists in the utilisation of compressed oxygen instead of air—this pro-

cess, and also a special apparatus for applying it, being patented by J. Bedford. The latter arrangement consists of a tank divided horizontally by partitions into shallow divisions, which communicate with each other only at alternate ends, and the oxygen, or air being fed into the lowest division, finds its way gradually upward through the apparatus. The oxidation is thus greatly facilitated, the process being much shortened and a better yield obtained.

Orchil is sold either in paste or powder form, the latter being known as *Cudbear*.

Orchil carmine is prepared by extracting the lichens with water, concentrating the solution to about 20° Tw., and adding about 10 per cent. of ammonia 0·88 specific gravity. The alkaline liquid is then aërated every day for six or seven weeks, when it gradually deposits a purple powder, which has about twice the colouring power of cudbear. The aëration may be brought about either by agitation or by allowing the liquid to flow in a thin stream from one vessel to another. The product is not much used.

"Fast Orchil."—This product is also little used. It is very similar to the "carmine," and is prepared as follows :—1 part of lichen is extracted with 20 parts of water, with a little ammonia, and to the solution is added stannate of soda in excess, which precipitates certain impurities. The clear liquor is then exposed to the air, and gradually deposits a purple precipitate, consisting of the tin lake of the colouring matter. When required for use it is dissolved in acetic or oxalic acid.

French purple is obtained by extracting the lichens with dilute ammonia and precipitating with hydrochloric acid. The precipitate is again dissolved in ammonia and the solution aërated, when it gradually acquires a bright red colour, which changes to purple on heating to 70° to 75° C. From this solution the colouring matter is precipitated by adding sulphuric or oxalic acid. Before adding to the dye-bath the colouring matter must be dissolved in ammonia.

CHEMISTRY OF ORCHIL.

The chemical changes which take place during the manufacture of orchil have been thoroughly investigated by Robiquet, Stenhouse, Schunck, and others.

The pure colouring matter of orchil is a purple body, *orcein*, which is produced during the manufacture from the colouring principle, *orcin*, by the combined action of oxygen and ammonia, according to the following equation—

$$C_7H_8O_2 + NH_3 + 3O = C_7H_7NO_3 + 2H_2O.$$
Orcin.   Orcein.
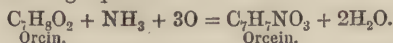
Orcin was first obtained by Robiquet in 1824, his method being to treat *Variolaria*

dealbata with alcohol, evaporate the extract to a syrup, treat this with water, and allow the concentrated aqueous solution of orcin to crystallise. It is also readily obtained in considerable quantity from *erythrin* (see below).

When pure, orcin forms colourless crystals, which are readily soluble in water, alcohol, or ether. From water it separates as the mono-hydrate ($C_7H_8O_2 . H_2O$).

Orcin is readily prepared from the coal-tar hydrocarbon *toluene* by the following series of reactions. Toluene is converted into chloro-toluene, which, by treatment with sulphuric acid for several hours at 100° C., is converted into two (α and β) isomeric *chloro-cresyl sulphonic acids*. The barium salts of these acids differ considerably in solubility, and they may therefore be separated by fractional crystallisation, the α acid being the useful product.

After conversion into its potassium salt the acid is fused with potassium hydrate, when it becomes brown, gives off hydrogen, and yields as principal product *orcin*, *cresol* and *salicylic* acid being also produced in small amount.

This method of formation shows that orcin is a dihydroxy toluene, $C_6H_3{<}{CH_3 \atop (OH)_2}$, from which its chemical properties may be inferred. It is interesting to note that orcin (and therefore orceïn) may be obtained from aloes by fusing the extract with caustic alkali.

Orcin does not pre-exist in many of the lichens, but is usually produced by the decomposition of certain original mother-substances found in the weeds. These vary according to the species of lichen from which they are obtained, but all possess the common property of yielding orcin under suitable decomposition. The following is a list of the chief of these mother-substances, but is by no means exhaustive:—

(1) *Erythrin or erythric acid*, $C_{20}H_{22}O_{10}$, a colourless crystalline body existing in *Roccella fuciformis*. In order to obtain it the weed is macerated with milk of lime, the solution filtered, and neutralised with hydrochloric acid. The precipitated erythrin is then washed and crystallised from alcohol. It is almost insoluble in water, but slightly soluble in alcohol or ether. With ferric chloride it gives a purple coloration. On boiling with dilute alkali the following decomposition occurs:—

$$C_{20}H_{22}O_{10} + H_2O = C_7H_8O_2 + C_{12}H_{16}O_7 + CO_2.$$
Erythrin.   Orcin.   Picroerythrin.

(2) *Lecanoric acid* (*Lecanorin, Orseillic acid*), $C_{16}H_{14}O_7$, a white crystalline substance, which yields orcin according to the equation—

$$C_{16}H_{14}O_7 + H_2O = 2C_7H_8O_2 + 2CO_2.$$
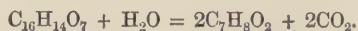
It exists in *Roccella tinctoria, Lecanora tartarea,* and *Variolaria orcina,* and may be prepared in a similar manner to erythrin. It is insoluble in water, but soluble in alcohol and ether.
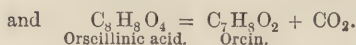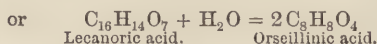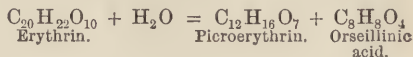
(3) *Usnic acid*, $C_{18}H_{18}O_7$, is found in *Usnea florida* and other species of *Usnea* and *Ramalina*. It is a bright yellow crystalline substance.

(4) *Evernic acid*, $C_{17}H_{16}O_7$, from *Evernia prunastri*, is a white crystalline body.

(5) *Cladonic acid*, $C_{18}H_{18}O_7$, is isomeric with *Usnic acid*, and has a similar appearance. Its chief source is *Cladonia rangiferina*.

Another substance may be here mentioned, which, like *orcin*, does not exist in the plants but is a decomposition product, viz. : —

Orseillinic Acid, $C_8H_8O_4$. It is produced as an intermediate product in the conversion of *erythrin* and *lecanoric acid* into *orcin*.

$$C_{20}H_{22}O_{10} + H_2O = C_{12}H_{16}O_7 + C_8H_8O_4$$
Erythrin.   Picroerythrin.   Orseillinic acid.

or $$C_{16}H_{14}O_7 + H_2O = 2C_8H_8O_4$$
Lecanoric acid.   Orseillinic acid.

and $$C_8H_8O_4 = C_7H_8O_2 + CO_2.$$
Orseillinic acid.   Orcin.

The preparation of orchil from the lichens thus consists in the extraction of the colour-yielding substances (*erythrin, lecanoric acid, usnic acid, evernic acid,* or *cladonic acid,* as the case may be), the production of the colouring principle (*orcin*) from these bodies by decomposition, with or without the intermediate formation of *orseillinic acid,* and the production of the colouring matter (*orcein*) from orcin by the simultaneous action of oxygen and ammonia. From this it will be seen that the first stages of the manufacture —the extraction of the active principle of the weeds and the production of orcin—should be modified according to the particular weed under treatment.

Adulterations.—Orchil extract is frequently adulterated with certain coal-tar colours with the object of strengthening or cheapening the product, and since these do not possess the special properties which make orchil valuable it is necessary to guard against their presence. The most common adulterant is a crude quality of magenta, which gives somewhat similar shades to orchil, and is a cheap product. Many other coal-tar colours, as well as logwood extract, have, however, been used for the purpose.

Testing Orchil and Cudbear.

Different samples of orchil extract or cudbear may vary much both in strength, brilliancy, and hue, without being purposely

adulterated. Frequent examination and comparison of examples should, therefore, be made, and this is most satisfactorily done by making careful comparative dyeing trials. In the case of orchil extract it is necessary to exercise great care that the sample withdrawn truly represents the bulk, because on long standing a very coherent cake is deposited at the bottom of the casks. The dyeing trials should be made upon woollen yarn or cloth, and with such an amount of colouring matter (say 5 to 10 per cent.) that a medium shade is obtained. The samples should be tested both in neutral and in acid baths, and a second lot of wool should be dyed in the liquors remaining after the first dyeing, in order to compare the exhaustion of the liquors; since different makes of orchil also vary much in this respect.

In an examination of samples for adulteration the process adopted will vary according to the nature of the suspected addition. For a complete scheme of qualitative analysis, reference may be made to an article by H. Breinl * ; but since a low quality of magenta is the most common adulterant, details for its detection are appended.

Breinl extracts the cudbear, or dried orchil, with alcohol, and precipitates the colouring matter from this solution by basic acetate of lead. After allowing the precipitate to settle, magenta is tested for in the clear liquid.

Rawson has improved this process by adding excess of ammonia after throwing down the orcein by acetate of lead, and as a means of estimating the amount of magenta in orchil this process is the best of many which have been proposed. It is carried out as follows:— Two grms. of cudbear, or dried orchil, are extracted with 60 c.c. alcohol, and to the extract, after diluting with 100 c.c. water, 20 c.c. basic acetate of lead solution 50° Tw., and then 20 c.c. strong ammonia, are added. After shaking, the solution is filtered, and 50 c.c. of the filtrate (which should be colourless) are acidified with acetic acid. If magenta is present, a pink or red colour is immediately developed, while with pure orchil the liquid remains colourless.

The amount of magenta present in the 50 c.c. of solution (= 0·5 grm. of the sample) may be estimated by comparing the depth of colour in a colorimeter with that of a solution of magenta of known strength. The presence of even 1 per cent. of magenta (on the weight of orchil) adds greatly to the fulness and brilliancy of the colour.

Logwood extract is another frequent adulterant found in orchil. It has little effect on the colour which is produced in the absence

* "Mitth. der Tech. Gewerbe Museum, Vienna," 1887, p. 37. Abstracted in *Journ. Soc. Dyers and Col.*, 1888, p. 46.

of any mordant, but orchil is frequently used in conjunction with chrome or alum mordant. In such cases 1 per cent. of logwood extract has a considerable influence upon the shade. This impurity is readily detected by dyeing a small piece of cotton prepared with a metallic mordant in a solution of the orchil.

APPLICATION OF ORCHIL AND CUDBEAR.

According to its chemical constitution orchil belongs to the class of phenolic colouring matters, being, as already noted, a dihydroxy toluene. As a class, the phenolic dyes require to be applied in conjunction with metallic mordants ; but although orchil may be so applied, it forms, like the eosin dyes, an exception to the rule, in that it may be used as a substantive dye. The colour-lakes formed by orcein with metallic bases are all similar in colour, which does not materially differ from the colour of the dye itself.

Orchil is usually applied to wool by the simple process of boiling the wool in a neutral or slightly acid solution of the colouring matter. The colour produced ranges from crimson-red to purple, the exact hue obtained being dependent partly upon the degree of acidity of the dye-bath. Two principal varieties of orchil are distinguished—"red orchil" and "blue orchil," these being obtained by variations in the process of manufacture, but any sample produces redder shades in an acid than in a neutral bath, orchil being affected by acids and alkalies in a similar manner to, but to a less extent than, the somewhat similar natural product litmus.

ORCHIL RED A (B.). An azo colour.

$$Xylidine < {Xylidine. \atop Beta\text{-}naphthol\ disulphonic \atop acid\ R.}$$

1879. Dark brown powder, giving a bluish-red solution in water. In concentrated H_2SO_4, dark blue solution ; on dilution, reddish-brown flakes.

Application.—An acid colour. Dyes *wool* orchil-red from an acid bath.

ORCHIL SUBSTITUTE G (Ber.). *Orchil extract G.* An azo dye.

$$Paranitraniline - {Beta\text{-}naphthylamine\ sul\text{-} \atop phonic\ acid\ Br.}$$

1885. Reddish-brown powder, soluble in water with a red colour. In concentrated H_2SO_4, red solution ; on dilution, brown ppt.

Application.—An acid colour. Dyes *wool* orchil-red from an acid bath.

ORCHIL SUBSTITUTE (or EXTRACT) N EXTRA (C.) *v.* APOLLO RED (G.).

ORCHIL SUBSTITUTE (or EXTRACT) V (Ber.) *v.* ORCHIL SUBSTITUTE 3 V N.

ORCHIL SUBSTITUTE (or EXTRACT) V (P.) (C.R.) (Fi.). *Naphthindone red.* An azo dye.

Paranitraniline — Naphthionic acid.

1878. Brown paste, soluble in water with a reddish - brown colour. In concentrated H_2SO_4, magenta-red solution; on dilution, brownish-red ppt.

Application.—An acid colour. Dyes *wool* and *silk* orchil-red from an acid bath.

ORCHIL SUBSTITUTE (or EXTRACT) 3 V N (P.). *Orchil substitute V* (Ber.). An azo colour.

Paranitraniline — $\begin{array}{l}\textit{Alpha-naphthylamine}\\\textit{sulphonic acid L.}\end{array}$

1887. Dark brown powder, giving a red solution in water. In concentrated H_2SO_4, brownish-red solution; unchanged on dilution,

Application.—An acid colour. Dyes *wool* and *silk* orchil-red from an acid bath.

ORCIN *v.* ORCHIL (CHEMISTRY OF).

ORSEILLINE B B (By.). An azo dye.

$\begin{array}{l}\textit{Amidoazotoluol sul-}\\\textit{phonic acid}\end{array} - \begin{array}{l}\textit{Alpha-naphthol sul-}\\\textit{phonic acid N W.}\end{array}$

1883. Brown powder, soluble in water with a magenta - red colour. In concentrated H_2SO_4, blue solution, which becomes magenta-red on dilution.

Application.—An acid colour. Dyes *wool* orchil-red from an acid bath.

ORIOL YELLOW (G.) *v.* ALKALI YELLOW (D.).

OXALATES *v.* OXALIC ACID.

OXALIC ACID, $C_2H_2O_4 = \begin{cases}CO(OH)\\CO(OH)\end{cases}$. The acid potassium salt exists in wood-sorrel, rhubarb, and some other plants.

Preparation.—Oxalic acid is made on the small scale by boiling sugar with dilute nitric acid. On concentrating the solution and cooling, crystals of the acid, containing 2 molecules of water ($C_2H_2O_4 + 2H_2O$), are formed.

The acid is manufactured by fusing sawdust with a mixture of caustic potash and caustic soda. The fused mass is extracted with water and the solution crystallised. The crystals are dissolved in water, and boiled with a slight excess of lime. The calcium oxalate formed is washed with water and boiled with sulphuric acid. The liquid is filtered, concentrated, and the oxalic acid crystallised. Re-crystallisation from hydrochloric acid, and afterwards from water, is necessary in order to obtain a pure product.

Properties.—Oxalic acid forms transparent monoclinic prisms. The crystals become anhydrous on heating to 100° C. By careful heating the acid can be sublimed, but at temperatures above 155° C. it is decomposed.

100 parts of water dissolve about 11 parts of oxalic acid at 15° C., and about 340 parts at 90° C.

Oxalic acid is a strong reducing agent, potassium permanganate decomposing it with formation of carbon dioxide.

The reaction takes place in presence of sulphuric acid, and more quickly when the solution is warmed.

$$5C_2H_2O_4 + 2KMnO_4 + 3H_2SO_4$$
$$= 10CO_2 + K_2SO_4 + 2MnSO_4 + 8H_2O.$$
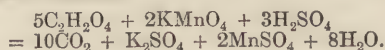
When oxalic acid is heated with glycerin to about 80° C. it is converted into formic acid, carbon dioxide being evolved.

$$\begin{cases}COOH\\COOH\end{cases} = H . COOH + CO_2.$$

Oxalic acid is a dibasic acid, and forms neutral salts, the so-called *oxalates*, and acid salts or *binoxalates*. The oxalates of the alkalies are soluble in water; most of the other oxalates are insoluble. Calcium oxalate is insoluble in acetic but easily soluble in hydrochloric or nitric acid. Oxalic acid and its compounds are poisonous.

Impurities.—The commercial acid sometimes contains organic matters, which cause the acid to turn black when treated with sulphuric acid. Lead and other heavy metals are occasionally present. Sulphates are often found in the acid.

Uses.—Oxalic acid is largely used in dyeing, as a discharge in calico printing, and for bleaching flax. It is a constituent of several dyes, and is employed for removing ink and iron stains from fabrics.

SPECIFIC GRAVITY OF SOLUTIONS OF OXALIC ACID, $H_2C_2O_4 + 2H_2O$, AT 15° (*Franz*).

Specific Gravity.	Per cent. $H_2C_2O_4 + 2H_2O$.	Specific Gravity.	Per cent. $H_2C_2O_4 + 2H_2O$.
1·0032	1	1·0226	8
1·0064	2	1·0248	9
1·0096	3	1·0271	10
1·0128	4	1·0289	11
1·0160	5	1·0309	12
1·0182	6	1·0320	12·6
1·0204	7		

Analysis.—*Commercial oxalic acid* is not very often found adulterated, and impurities due to careless manufacture are not, as a rule, great. The amount of pure acid (in the absence of other acids and acid salts) may be accurately determined by standard alkali and phenolphthaleïn. 2 grms. is a convenient quantity to take for titration.

1 c.c. $\frac{N}{1}$ NaOH = 0·063 grm. crystalline oxalic acid, $C_2H_2O_4$, $2H_2O$.

Oxalic acid and oxalates may be determined in several ways by conversion in the

first place into calcium oxalate. In the absence of other acids which are precipitated by calcium salts, the liquid may be neutralised by ammonia and calcium chloride added. If phosphates, tartrates, sulphates, &c., are present the solution must be made slightly acid with acetic acid before adding the calcium chloride. The calcium oxalate obtained may be converted into calcium carbonate by gentle ignition, and weighed as such; or it may be converted into calcium sulphate. It is better, however, to proceed according to one of the following methods :—

1. Wash the calcium oxalate well with hot water, transfer it to a crucible and ignite. The oxalate is converted into carbonate and, possibly, partly into oxide; but the results are the same in either case. The ignited residue is treated with an excess of normal nitric acid, the liquid warmed until solution is effected, and, using methyl-orange as indicator, the cooled liquid is titrated back with normal caustic soda.

1 c.c. $\frac{N}{1}$ acid consumed = 0·063 grm. $C_2H_2O_4, 2H_2O$.

2. Instead of drying and igniting the calcium oxalate, it may be transferred direct to a beaker, treated with water and dilute sulphuric acid, and titrated with potassium permanganate as described below.

Titration of Oxalic Acid and Oxalates by Permanganate.—In the absence of other oxidisable bodies, this forms a ready means of estimating oxalic acid either free or combined. A decinormal solution of potassium permanganate, containing 3·16 grms. of $KMnO_4$ per litre, is prepared by taking rather more than that amount of the salt and standardising the solution with *pure* oxalic acid. For this purpose exactly 0·315 grm. of pure oxalic acid (or 50 c.c. of $\frac{N}{10}$ solution) is taken and dissolved in about 50 c.c. of water. About 50 c.c. of 10 per cent. sulphuric acid are added, the liquid heated to about 55° C. and titrated while hot with $\frac{N}{10}$ permanganate until a permanent pink colour appears. If the permanganate is strictly decinormal 50 c.c. will be required to produce this effect. If found to be too strong, it is diluted in the same manner as described under standard solution of sulphuric acid (p. 11). The sample of oxalic acid or oxalate to be determined is then treated in exactly the same way.

1 c.c. $\frac{N}{10}$ $KMnO_4$ = 0·0063 grm. $C_2H_2O_4, 2H_2O$.

Impurities in Oxalic Acid.—*Mineral salts* are detected by igniting a portion of the sample ; *sulphates* by dissolving in water and adding barium chloride and hydrochloric acid. *Organic matter*, other than oxalic acid,

is present if the sample blackens on heating alone, or with concentrated sulphuric acid.

OXAMINE BLACK B R (B.). 1897. A direct black cotton dye.

OXAMINE BLUE 3 R (B.). An azo dye.

Tolidine { Beta-amido alpha-naphthol alpha-sulphonic acid. / Alpha-naphthol sulphonic acid *N W*.

1893. Brownish-violet powder, soluble in water with a violet colour. In concentrated H_2SO_4, bright blue solution ; on dilution, violet ppt.

Application.—A direct cotton colour. Dyes *cotton* violet-blue from an alkaline salt bath.

OXAMINE BLUE B, R, R X, 3 R (B.), **OXAMINE GREEN M** (B.), **OXAMINE MAROON, OXAMINE SCARLET,** have also been introduced.

OXAMINE RED (B.). Brown powder. Aqueous solution, brownish-red ; alcoholic solution, orange-red. Concentrated H_2SO_4, bright blue ; on dilution, brownish-red.

Application.—A direct cotton dye, giving bluish-red shades.

OXAMINE VIOLET (B.). An azo dye.

Benzidine { Beta-amido alpha-naphthol beta-sulphonic acid. / Beta-amido alpha-naphthol beta-sulphonic acid.

1893. Blackish glistening powder, giving a red-violet solution in water. In concentrated H_2SO_4, bright blue solution ; on dilution, violet ppt.

Application.—A direct cotton colour. Dyes *cotton* reddish-violet from an alkaline salt bath.

OXYCELLULOSE *v.* COTTON (CELLULOSE).

OXYDIAMINE BLACK N (C.). An azo dye. Black powder. Insoluble in cold water ; in alcohol, reddish-blue solution. Concentrated H_2SO_4, bright blue ; on dilution, reddish-blue.

Application.—A direct cotton colour. Dyes *cotton* black from an alkaline sodium sulphate bath. By subsequent treatment with *copper sulphate* shade becomes faster to washing.

OXYDIAMINE BLACK N R (C.). Is a similar colour.

OXYDIAMINE BLACK S O O O (C.). Brownish-black powder. Aqueous solution, dull blue ; alcoholic solution, reddish-blue. Concentrated H_2SO_4, bright blue ; on dilution, reddish-blue solution with brown ppt., which re-dissolves.

Application.—A direct cotton colour. Dyes *cotton* black from an alkaline sodium sulphate bath. May be azotised on the fibre and developed with *beta-naphthol* or *phenylene diamine*.

OXYGEN POWDER *v.* SODIUM PEROXIDE.

OXYMURIATE OF TIN v. TIN SPIRITS.

OXYPHENINE (Clayton Co.) v. CHLOR-AMINE YELLOW (By.).

P

PACIFIC BLUE B, 4 B (H.). Direct cotton blues.

PAEONINE v. CORALLINE.

PALATINE CHROME BLACK A (B.). 1899. An acid black for wool, fixed by saddening with bichromate of potash.

PALATINE ORANGE. An obsolete nitro compound dyeing *wool* orange from an acid bath.

PALATINE RED (B.). *Naphthorubin* (By.) (M.). An azo dye.

$$Alpha\text{-}naphthylamine - Alpha\text{-}naphthol\ di\text{-}sulphonic\ acid\ R\ G$$

1886. Greyish-blue powder, giving a bluish-red solution in water. In concentrated H_2SO_4, blue solution; on dilution, brown ppt.

Application.—An acid colour. Dyes *wool* or *silk* bluish-red from an acid bath.

PALATINE SCARLET (B.). *Cochineal scarlet P S* (By.). An azo dye.

$$Metaxylidine - Alpha\text{-}naphthol\ disul\text{-}phonic\ acid\ R\ G.$$

1886. Brownish-red powder, giving a yellowish-red solution in water. In concentrated H_2SO_4, cherry-red solution, becoming slightly more crimson on dilution.

Application.—An acid colour. Dyes *wool* scarlet-red from an acid bath.

PALMITIC ACID, $C_{16}H_{32}O_2 = C_{15}H_{31}$ $(CO \cdot OH)$, is a white substance which melts at $62°$ C., and can be distilled under diminished pressure without being decomposed. It is a monobasic acid, the salts of which are called *palmitates*. Potassium and sodium palmitates are the chief constituents of palm oil soap; they are decomposed by water (v. SOAP). The other salts are insoluble in water.

Palmitin or Tripalmitin, $(C_{16}H_{31}O_2)_3$ C_3H_5, is the glycerin ether of palmitic acid. It occurs in most animal fats, in olive oil and in palm oil, and melts at $66°$ C. Palmitin is decomposed into glycerin and palmitic acid, or a palmitate, on being heated with sulphuric acid, alkalies, lime, or superheated steam. The process of decomposition with alkali of this and similar ethers is called *saponification*, and the resulting salt *soap*. Soaps made from palmitic acid are used by dyers.

"PANAMA CRIMSON" is obtained from the leaves of a vine called *china*, and is employed in the country of its origin for dyeing straw hats a bright crimson, which is stated to be fast to light.

PAPER SCARLET BLUE SHADE (M.) v. BRILLIANT CROCEINE M (C.).

PARA BLUE (N.J.). A basic induline. 1890. Blue powder, soluble in water. In concentrated H_2SO_4, blue solution; on dilution, bright blue ppt.

Application.—A basic colour. Dyes tannin-mordanted *cotton* greyish-blue.

PARAFFIN (ESTIMATION OF) v. ANTHRACENE.

PARAFFIN WAX v. SIZES.

PARANITRANILINE RED v. AZO COLOURS ON COTTON.

PARAPHENYLENE BLUE R (D.). *Fast new blue for cotton.* A basic induline. 1886. Dark grey powder, soluble in water with a blue colour. In concentrated H_2SO_4, blue solution, which is unchanged on dilution.

Application.—A basic colour. Dyes tannin-mordanted *cotton* blue, which becomes darker and faster by subsequent oxidation with bichromate of potash.

PARAPHENYLENE VIOLET (D.). A basic induline. 1886. Dark bronzy powder, soluble in water with a violet colour. In concentrated H_2SO_4, green solution, which becomes first blue and then violet on dilution.

Application.—A basic colour. Dyes tannin-mordanted *cotton* violet.

PARAROSANILINE v. ROSANILINE.

PARASULPHURINE S v. SULPHANIL YELLOW.

PARIS GREEN. Old name for METHYL GREEN.

PARIS GREENS. Obsolete basic greens, obtained by oxidising *benzylaniline*, &c.

PARIS VIOLET v. METHYL VIOLET.

PARMA R v. PRUNE PURE.

PARMA VIOLET = *Mono* and *diphenyl rosaniline* (obsolete).

PARSLEY contains a colouring matter which has been investigated by Linderhorn, A. G. Perkin, and others, and the latter chemist considers it to be closely allied to *chrysin*, the dyeing principle of poplar buds.[*] Both these products yield fine yellow shades on wool, in conjunction with alum mordant.

PATENT ALUM v. ALUMINIUM SULPHATE.

PATENT BARK v. QUERCITRON BARK.

PATENT BLUE A (M.). A rosaniline derivative. *Calcium salt of metoxy-diethyl-dibenzyl diamidotriphenyl carbinol disulphonic acid.* 1888. Coppery-looking powder, soluble in water with a blue colour. In concentrated H_2SO_4, yellow solution, which becomes green on dilution.

Application.—An acid colour. Dyes *wool* and *silk* bright blue from an acid bath.

PATENT BLUE V, N, Concentrated, and Superfine (M.). Similar to above.

[*] "Apiin and Apigenin," *Trans. Chem. Soc.*, 1897, p. 805.

Calcium (or sodium) salt of metoxy-tetrethyl diamido triphenyl carbinol disulphonic acid. 1888. Copper-red powder, soluble in water with a bright blue colour. In concentrated H_2SO_4, yellow solution, which becomes green on great dilution.

Application.—An acid colour. Dyes *wool* and *silk* greenish-blue from an acid bath.

PATENT FUSTINE O (Wood & Bedford). *Wool yellow* (B.). An azo compound.

Aniline — Maclurin (Fustic extract).

1887. Brownish-yellow paste or powder, nearly insoluble in water. In concentrated H_2SO_4, reddish-brown solution ; on dilution, yellowish-brown ppt.

Application.—An acid-mordant dye. Dyes *wool* direct from an acid bath, or chrome-mordanted *wool* from a neutral bath, giving a reddish-brown shade.

PATENT GREEN V (M.). Violet powder. Aqueous and alcoholic solution, greenish-blue. Concentrated H_2SO_4, brownish-red solution ; on dilution, greenish-yellow, then bright green.

Application.—An acid colour, giving bluish-green shades on *wool* or *silk.*

PATENT ORANGE (Ber.) v. ORANGE G (Ber.).

PATENT PHOSPHINE (S.C.I.) v. PHOSPHINE.

PATENT ROCK SCARLET (Br. S.) v. SAINT DENIS RED (P.).

PEACHWOOD v. REDWOODS (SOLUBLE).

PECTIC ACID v. COTTON (IMPURITIES IN RAW).

PECTOCELLULOSE v. COTTON.

PEGU BROWN (L.). A direct cotton brown.

PELICAN BLUE v. INDULINE.

PERKIN'S VIOLET v. ROSOLANE (P.).

PERMANENT WHITE v. BARIUM SULPHATE.

PERMANGANATE OF POTASH v. MANGANESE OXIDE.

PERNAMBUCO WOOD v. REDWOODS (SOLUBLE).

PEROXIDE OF HYDROGEN v. HYDROGEN PEROXIDE.

PERSIAN BERRIES.

Origin.—This dyestuff is the fruit of several species of *Rhamnus*, and grows in Persia, Turkey, Spain, and several other parts of Europe. The true *Persian* berries are from *R. infectoria* and *R. tinctoria*, and are principally cultivated in Europe.

The berries are gathered before they are quite ripe, and when of good quality they possess a dark green colour and are hard. When ripe they are yellow in colour and are inferior, as also are such as have a brown or black appearance, which indicates that the colouring matter has been partially decomposed.

The berries are sold without any previous preparation, but before use are ground to powder. If stored in the ground condition, they rapidly deteriorate.

Colouring Matters of Persian Berries.—The berries appear to contain at least two glucosides. Under the name *xantho-rhamnin* (latterly *alpha-rhamnin*) one of these has been known for a considerable time, being first obtained by Gellatly, 1858. The second glucoside was isolated by Schützenberger, who named it *beta-rhamnegin.*

When boiled with dilute mineral acid, *alpha-rhamnegin* yields *iso-dulcitol* and a colouring matter, *rhamnetin*, while under similar conditions *beta-rhamnegin* produces iso-dulcitol and *quercetin.*

Further, it has been shown by Herzig that *rhamnetin* is a *monomethyl ether of quercetin*, and Perkin has prepared from Persian berries a *quercetin dimethyl ether*, to which he has given the name *rhamnazin.*

Persian berries thus contain at least three colouring matters—viz., *quercetin* ($C_{15}H_{10}O_7$), *rhamnetin* ($C_{16}H_{12}O_7$), or quercetin monomethyl ether, and *rhamnazin* ($C_{17}H_{14}O_7$), or quercetin dimethyl ether. *Rhamnetin* is the principal colouring matter.

The various colouring matters may be prepared as follows [*] :—Ground Persian berries are extracted with water, and from the orange-brown solution thus obtained a yellow precipitate soon separates. This is collected, washed with water, and dried. The dry powder is then extracted with boiling toluene, which on cooling deposits impure *rhamnazin.* The residue, insoluble in toluene, is dissolved in boiling alcohol, from which a crystalline mass of *rhamnetin* is deposited on partial evaporation.

The alcoholic liquor, on considerable further evaporation, yields the *quercetin*, a quantity of which substance may also be obtained from the original aqueous mother-liquor.

The various products may be further purified by crystallisation, *rhamnazin* from acetic acid and toluene, *rhamnetin* from acetic acid, and *quercetin* from a mixture of ether and chloroform. All three bodies crystallise in yellow needles.

Application.—Persian berries are not used in wool dyeing, but in the form of extract and carmine are employed in *calico* printing.

PERSIAN BERRY EXTRACT is prepared in a similar manner to logwood extract.

PERSIAN BERRY CARMINE or DUTCH YELLOW is a pigment consisting of the aluminium and calcium lakes of the Persian berry colouring matters.

PERSIAN YELLOW (G.). An azo dye.

Nitro-paratoluidine — Salicylic acid.

1888. Brownish-yellow paste, soluble in

[*] A. G. Perkin, *Journ. Chem. Soc. Trans.*, 1895, p. 495.

boiling water with a yellow colour. In concentrated H_2SO_4, orange-yellow solution; on dilution, brownish-yellow ppt.

Application. — A mordant dye. Dyes chrome-mordanted *wool* yellow.

PERSULPHOCYANOGEN YELLOW v. CANARIN.

PETROLEUM SPIRIT, PETROLEUM BENZENE, BENZINE, and LIGROÏN are the light oils of American petroleum, and consist chiefly of the saturated hydrocarbons of the fatty series, which correspond to the general formula $C_n H_{2n+2}$. They possess a specific gravity of 0·65 to 0·75, and boil from 50° to 120°; the lightest of these oils is called petroleum spirit, the heaviest ligroïn.

PHENAMEINE } v. ROSOLANE.
PHENAMINE }

PHENANTHRENE v. ANTHRACENE.

PHENETOL RED. *Coccinine* (M.). An obsolete acid azo colour.

PHENICIENNE. *Phenicine.* v. PHENYL BROWN.

PHENOCYANINE B, R, TV, TB (D. & H.). Oxazine dyes, obtained by the condensation of *oxazines* with *resorcinol*. 1894. Greenish-yellow paste, insoluble in water. In concentrated H_2SO_4, brown solution; on dilution, brown ppt.

Application. — Mordant dyes which require oxidation to develop the colour. With chrome mordant they give blue colours.

PHENOFLAVIN (O.). An azo dye.

Metanilic acid — *Amidophenol sulphonic acid III.*

1892. Brownish-yellow powder, soluble in water. In concentrated H_2SO_4, yellow solution; unchanged on dilution.

Application. — An acid colour. Dyes *wool* yellow from an acid bath.

PHENOL (*Carbolic acid*), $C_6 H_5 (O H)$, occurs in coal tar. It forms, in the pure state, a colourless crystalline mass, which becomes gradually reddish, and deliquesces in the air.

Preparation. — Phenol is obtained from the coal-tar oils which boil between 170° and 230° C. This fraction is treated with soda lye of 1·095 specific gravity in iron tanks at about 45° C. for two hours, with continual agitation. The lower stratum (after being allowed to settle) consists of sodium phenolate, which is drawn off and treated with dilute acid (generally sulphuric) in excess in lead-lined vessels, the aqueous liquor being run off while still hot to prevent crystallisation. The crude carbolic acid which formed the supernatant layer is purified by distillation and subsequent fractionation or crystallisation.

Properties. — Phenol melts at 42° C. and boils at 180° C. It has the specific gravity 1·065 at 18° C. According to Lunge ordinary "pure" carbolic acid melts at 35° and boils at 183° C. Small amounts of water or heavy hydrocarbons cause a considerable lowering of the melting point.

Carbolic acid possesses a peculiar smell and a burning taste, is very poisonous, and is antiseptic. It dissolves in 15 parts of water at 20° C., and very freely in alcohol, ether, and glacial acetic acid.

Reactions. — Phenol forms salts with metallic bases, such as sodium phenolate (C_6H_5ONa); the salts are decomposed by the weakest acids, even by carbonic acid.

Carbolic acid dissolves readily in caustic soda, forming the phenolate or phenate of soda.

Neutral solutions of phenol are coloured violet by ferric salts. On gently heating an aqueous solution of phenol with ammonia, and adding a drop of sodium hypochlorite, a deep blue colour (green in dilute solutions) is produced, which is changed to red by acids.

Bromine water precipitates the yellowish-white tribromophenols from solutions, even when highly diluted.

Analysis. — *Water* is estimated in crude carbolic acid (*i.e.*, the liquid remaining after crystallisation of the phenol, and consisting of cresol and higher homologues) by several methods.

J. A. Wilson [*] gives the following comparative results, obtained by testing a sample by three methods :—(No. 1) By distillation, the volume of the water passing over being measured ; (No. 2) by agitating one volume with three volumes of saturated salt solution ; (No. 3) by agitating with equal volumes of 50 per cent. sulphuric acid ;

	No. 1.	No. 2.	No. 3.
Water,	8·60	8·00	8·25 per cent.

Phenol is estimated by H. Beckurt [†] by mixing a given volume of the sample with an equal volume of petroleum-ether, and shaking up the whole with a definite volume of excess of 10 per cent. soda-lye. A complete separation of the alkaline liquid from the hydrocarbons ensues within ten minutes. The volume of the matter insoluble in soda, less the volume of the petroleum-ether added, shows the volume of the neutral oils present.

Estimation of Phenol in Raw Products. — Töth's modification of Koppeschaar's process is recommended by Sutton.[‡] 20 c.c. of the impure carbolic acid are placed in a beaker with 20 c.c. of caustic potash solution of 1·3 specific gravity, well shaken, and allowed to stand for half an hour, then diluted to about ¼ litre with water. By this treatment the foreign impurities are set free, and may

[*] *Chem. News*, vol. lxi., p. 236.
[†] *Ibid.*, vol. lvii., p. 92.
[‡] *Volumetric Analysis*, seventh edition, p. 367.

mostly be removed by filtration ; the filter is washed with warm water until all alkali is removed. The filtrate and washings are acidulated slightly with HCl, and diluted to 3 litres. 50 c.c. are then mixed with 150 c.c. of standard bromine solution, and then 5 c.c. concentrated HCl. After twenty minutes, with frequent shaking, 10 c.c. of potassium iodide solution are added, mixed and allowed to rest five minutes, then starch paste, and the titration with $\frac{N}{10}$ sodium thiosulphate carried out as usual.

Example.—20 c.c. raw carbolic oil were treated as above described. 50 c.c. of the solution, with 150 c.c. bromine solution (made by dissolving 2·04 grms. sodium bromate and 6·96 grms. sodium bromide per litre), then 5 c.c. of HCl, required 17·8 c.c. of thiosulphate for titration. The 150 c.c. bromide = 0·237 grm. Br. The 17·8 c.c. thiosulphate required for residual titration = 0·052 grm. Br, leaving 0·185 grm. Br for combination with the phenol.

According to the equation—

$$C_6H_5OH + 3Br_2 = 3HBr + C_6H_2Br_3OH,$$
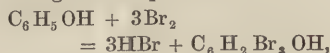
1 molecule phenol = 3 molecules Br, hence the percentage of phenol was 10·86.

In titrating acid creosote oil by the bromine method, an error will be incurred owing to phenols of higher molecular weight than carbolic acid acting in the same manner with bromine as the phenol itself.

PHENOL BLACK SS, PHENOL BLUE-BLACK 3 B (By.). Acid dyes for *wool.*

PHENOLPHTHALEÏN (Indicator) *v.* ACIDIMETRY.

PHENOLPHTHALEÏN—

$$C_6H_4 . OH \atop C_6H_4 . OH > C < {C_6H_4 . CO \atop O———}$$
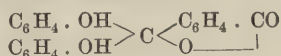
Obtained by heating *phenol* with *phthalic anhydride.* 1871. Yellow crystals or buff-coloured powder, insoluble in water, but soluble in alcohol. In concentrated H_2SO_4, yellowish-brown solution precipitated on dilution.

Application.—Not used as a dye but as an indicator in volumetric analysis. Its alkali salts have an intense red colour.

PHENOSAFRANINE *v.* SAFRANINE B Extra (B.).

PHENYL BROWN. *Phenicine, Phenicienne, Rotheine.* An obsolete nitro compound used in leather dyeing.

PHENYLENE BLACK (P.) *v.* ANTHRACITE BLACK B (C.).

PHENYLENE BLUE *v.* NEW BLUE.

PHENYLENE BROWN *v.* BISMARCK BROWN.

**PHENYLENE DIAMINE,** $C_6H_4(NH_2)_2$. Used as a developer in dyeing with certain direct cotton colours. It is insoluble in water, but its salts, particularly the hydrochloride, are soluble.

PHILADELPHIA YELLOW G (Ber.) *v.* PHOSPHINE.

PHLOBAPHANES. The term *phlobaphane* was first applied to a substance obtained from oak tannin by the action of dilute acid or alkali, which differed from the original tannin in several respects, being soluble in water and having a red colour. This body was shown to be an anhydride of the tannin, and the term is now used generically to designate the anhydrides of the various tannic acids formed by the removal of one or more molecules of water from one or more molecules of the tannin.

The phlobaphanes are produced by boiling aqueous solutions of the tannins with dilute sulphuric acid. They also exist naturally in oak bark, &c., in conjunction with the tannins, constituting the colouring matters in tannin substances. They are red or brown amorphous bodies which are insoluble in cold water, but slightly soluble in boiling water. They have similar reactions to the tannins, are useful in leather manufacture, but injurious in tannins employed for fixing basic coal-tar dyes on account of their dark colour.

PHLOROGLUCINOL,

$$C_6H_3 \begin{cases} OH \ (2) \\ OH \ (4) \\ OH \ (6) \end{cases}$$
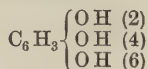
(Phloroglucin),

is isomeric with pyrogallol and metagallic acid. It is produced by the action of caustic potash on *catechu, maclurin* (from old fustic), *quercitannic acid* (from oak bark), and other tannin substances. It crystallises with two molecules of water, which are given off at 100° C. It melts at from 209° to 218° C. It is easily soluble in water, alcohol, and ether, and its solutions have a sweet taste. It gives a precipitate with basic lead acetate, but not with other metallic salts. With ferric chloride it produces a violet coloration, and, like other phenols, is readily oxidisable.

PHLOXINE (M.) (Ber.). *Phloxine T A* (Mo.), *Cyanosine* (D. & H.), *Eosine 10 B* (C.), *Eosine blue shades.* A phthaleïn derivative. *Sodium salt of tetrabrom tetrachlor fluoresceïn.* 1882. Brick-red powder, giving in water a bluish-red solution with dark green fluorescence. In concentrated H_2SO_4, yellow solution, which, on dilution, deposits yellowish-red flocks.

Application.—An acid dye (on wool) or a mordant dye (on cotton). Dyes *wool* or *silk* a bluish-pink or red from a slightly acid bath. *Cotton* is mordanted with lead, tin, or aluminium.

PHLOXINE P (B.). *Phloxine* (C.) (M.) (F.) (D. & H.), *Erythrosine B B* (Ber.), *New pink.* A phthaleïn derivative. *Potassium salt of tetrabrom dichlor fluorescein.* 1875. Brownish-yellow powder, soluble in water with a cherry-red colour with greenish-yellow fluorescence. In concentrated H_2SO_4, yellowish-brown solution, which gives a dark brown ppt. on dilution.
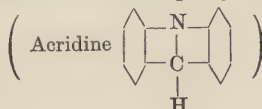
Application.—v. PHLOXINE.

PHLOXINE T A (Mo.) *v.* PHLOXINE.

PHŒNIX RED A (C.).

PHOSPHINE (many makers). *Phosphine II* (C.), *Phosphine N and P* (K.), *Xanthine* (P.) (L.) (D. & H.), *Philadelphia yellow G* (Ber.), *Leather brown* (M.), *Leather yellow* (M.) (D.) (L.) (D. & H.), *Chrysaniline.* An acridine derivative. Produced as a by-product in the manufacture of magenta. *Mixture of salts of chrysaniline and chrysotoluidine.*

Chrysaniline = Diamido phenyl acridine.

$$\left(\text{Acridine} \begin{array}{c} \diagup\diagdown - \text{N} - \diagup\diagdown \\ \diagdown\diagup - \underset{|}{\text{C}} - \diagdown\diagup \\ \text{H} \end{array} \right)$$

Orange-yellow powder, giving a reddish-yellow solution in water. In concentrated H_2SO_4, reddish-yellow solution, with green fluorescence; unchanged on dilution.

Application.—A basic colour, chiefly employed in the dyeing of leather.

PICRIC ACID (many makers). A nitro compound. *Trinitro phenol.* Obtained in 1771 (from indigo), 1799 (from silk), 1842 (from phenol), 1869 (from phenol sulphonic acid). Lemon-yellow crystals, soluble in water. Its solution has a very bitter taste. In concentrated H_2SO_4, greenish-yellow solution, which ppts. on dilution.

Picric acid and the picrates are highly explosive when heated.

Application.—An acid colour. Dyes *wool*, *silk*, and *leather* greenish-yellow from an acid bath. Used also in preparing orthochromatic photographic plates, and, very largely, in the manufacture of smokeless explosives.

PIGMENT BROWN (B.). *Sudan brown* (Ber.) (Fi.). An azo compound.

Alpha-naphthylamine — Alpha-naphthol.

1878. Brown powder, insoluble in water, but soluble in alcohol. In concentrated H_2SO_4, blue solution; on dilution, brown ppt.

Application. — Used in colouring spirit lakes, soaps, &c.

PINCOFFIN *v.* MADDER (PREPARATIONS).

PINK. Old name for SAFRANINE.

PINK CUTTING LIQUOR *v.* TIN SPIRITS.

PINK SALT *v.* TIN COMPOUNDS.

PITTAKEL. An obsolete *aurine* derivative.

PLUMBATES *v.* LEAD HYDROXIDE.

PLUMBITES *v.* LEAD CHROMATES.

PLUM SPIRITS *v.* TIN SPIRITS.

PLUTO BLACK F R (By.). 1899. A direct cotton dye. Dyes unmordanted *cotton* or *union* material black.

PLUTO BROWN N B, G G, R (By.). 1898. Direct cotton dyes. Dye unmordanted *cotton* brown, which is rendered darker by developing with "nitrol" (diazotised paranitraniline).

PŒONINE *v.* CORALLINE.

POISONS, ANTIDOTES FOR, *v.* ANTIDOTES.

POLYCHROMINE (G.) *v.* PRIMULINE.

POLYCHROMINE B (G.). *Cotton brown R* (G.), *Fast cotton brown R* (G.), *Direct brown R* (G.). An azo colour.

$$\text{Diamidostilbene disulphonic acid} < \begin{array}{c} \text{Aniline.} \\ \text{Aniline.} \end{array}$$

1890. Brown powder, soluble in water with an orange-brown colour. In concentrated H_2SO_4, cherry-red solution; on dilution, blue-black ppt.

Application.—A direct cotton colour. Dyes *cotton* yellowish-brown from a neutral bath. By subsequent diazotisation and development various colours are produced; with *beta-naphthol*, claret-red; with *phenylene diamine*, brown.

POLYPHENYL BLACK B (G.). 1899. A direct cotton black.

POLYPHENYL YELLOW R (G.). 1899. A direct cotton yellow.

POMONA GREEN *v.* IODINE GREEN.

PONCEAU. Synonym of SCARLET.

PONCEAU B (M.) *v.* PONCEAU 3 R B (Ber.).

PONCEAU B O EXTRA (Ber.) *v.* BRILLIANT CROCEÏNE M (C.).

PONCEAU G (C.) (Lev.) (M.) *v.* PONCEAU 2 R.

PONCEAU 2 G (Ber.) (B.) (M.). *Brilliant ponceau G G* (C.), *Ponceau J J.* An azo dye.

$$\text{Aniline} - \begin{array}{c} \text{Beta-naphthol disulphonic} \\ \text{acid R.} \end{array}$$

1878. Bright red powder, soluble in water. In concentrated H_2SO_4, cherry-red solution, changing to yellowish-red on dilution.

Application.—An acid colour. Dyes *wool* and *silk* red-orange from an acid bath.

PONCEAU 4 G B (Ber.) *v.* CROCEÏN ORANGE (By.).

PONCEAU G R (M.) *v.* PONCEAU 2 R.

PONCEAU J *v.* PONCEAU 2 R.

PONCEAU J J *v.* PONCEAU 2 G.

PONCEAU R (M.) (Ber.) *v.* PONCEAU 2 R.

PONCEAU 2 R (Ber.) (B.) (Lev.) (F.) (M.) (P.). *Ponceau G* (Lev.) (M.), *Ponceau G R* (M.), *Ponceau R* (M) (Ber.), *Ponceau J, Brilliant ponceau G* (C.), *Xylidine red,* *Xylidine scarlet.* An azo dye.

Xylidine — *Beta-naphthol disulphonic acid R.*

1878. Brownish - red powder, soluble in water. In concentrated H_2SO_4, cherry-red solution, which, on dilution, becomes reddish-yellow.

Application.—An acid colour. Dyes *wool* and *silk* red from an acid bath. Used also in lake making.

PONCEAU 3 R and 4 R (M.) (B.) (Ber.). *Cumidine red, Cumindine ponceau.* An azo compound.

ψ-Cumidine — *Beta-naphthol disulphonic acid R.*

1878. *Ponceau 4 R* is a pure product. Dark red powder, soluble in water with a cherry-red colour. In concentrated H_2SO_4, cherry-red solution, unchanged on dilution.

Application.—*v.* PONCEAU 2 R.

PONCEAU 3 R B (Ber.). *Ponceau B extra* (M.), *Fast Ponceau B* (B.), *New red L* (K.), *Biebrich scarlet* (K.), *Scarlet E C* (C.), *Imperial scarlet* (By.), *Scarlet B* (P.). An azo dye.

Amidoazobenzol disulphonic acid — *Beta-naphthol.*

1879. Reddish-brown powder, giving a yellowish-red solution in water. In concentrated H_2SO_4, green solution; on dilution, first blue solution, then bluish-red ppt.

Application.—An acid colour. Dyes *wool* and *silk* red from an acid bath.

PONCEAU 4 R B (Ber.) *v.* CROCEÏN SCARLET 3 B (By.).

PONCEAU 5 R (M.). *Erythrin X* (B.). An azo dye.

Amidoazobenzol — *Beta-naphthol trisulphonic acid.*

1881. Brown powder, soluble in water with a cherry-red colour. In concentrated H_2SO_4, reddish-violet solution, becomes first blue, and then red on dilution.

Application.—An acid colour. Dyes *wool* and *silk* bluish-red from an acid bath. Used also in colouring paper pulp.

PONCEAU 6 R (M.) (B.). *Scarlet 6 R.* An azo dye.

Naphthionic acid — *Beta-naphthol trisulphonic acid.*

1881. Brown powder, giving a magenta-red solution in water. In concentrated H_2SO_4, violet solution, which becomes magenta-red on dilution.

Application.—An acid colour. Dyes *wool* or *silk* red from an acid bath. The colour is fast to light

PONCEAU 6 R B (Ber.) *v.* CROCEÏN SCARLET 7 B (By.).

PONCEAU 10 R B (Ber.). Reddish-brown powder. Aqueous or alcoholic solution, bluish - red. Concentrated H_2SO_4, bright blue; on dilution, reddish-blue, then bluish-red.

Application.—An acid colour. Dyes *wool* or *silk* bluish-crimson from an acid bath.

PONCEAU R T. An azo dye.

Toluidine — *Beta-naphthol disulphonic acid R.*

1878. Red powder, soluble in water. In concentrated H_2SO_4, cherry-red solution, becoming yellowish-red on dilution.

Application.—An acid colour. Dyes *wool* and *silk* reddish-orange from an acid bath.

PONCEAU S EXTRA (Ber.) *v.* FAST PONCEAU 2 B (B.).

PONCEAU 2 S EXTRA (Ber.). An azo dye.

Amidoazo benzene — *Beta-naphthol disulphonic acid R.*

1879. Brown powder, soluble in water with a magenta-red colour. In concentrated H_2SO_4, violet solution; on dilution, violet ppt.

Application.—An acid colour. Dyes *wool* and *silk* red from an acid bath.

POPPY FLOWERS (*Papaver rhœas*) contain a red colouring matter used in colouring wines and in pharmacy. It is not poisonous.

POTASHES *v.* POTASSIUM CARBONATE.

POTASSIUM, K = 39. Potassium is found in combination in *saltpetre* (KNO_3), in the ashes of plants as K_2CO_3 (crude potashes), and in some silicates and sulphates. Saline deposits of the chloride occur at Stassfurth in Germany. The metal has a brilliant silver - white lustre when freshly cut, but quickly tarnishes in the air, forming an oxide. It decomposes water with formation of potassium hydrate, and liberation of hydrogen. The metal itself is of little practical importance, but its compounds are largely used in many industries.

POTASSIUM ANTIMONY TARTRATE *v.* TARTAR EMETIC.

POTASSIUM ARSENATE, KH_2AsO_4, obtained by fusing white arsenic and potassium nitrate, lixiviating and crystallising. It is used as a dung substitute in calico printing.

POTASSIUM BITARTRATE, ACID POTASSIUM TARTRATE, $C_4H_4O_4(OH)(OK)$. *Cream of Tartar, Tartar, Argol.*—This substance occurs, together with other organic acids in mulberries, sorrel, and in considerable quantity in the juice of the grape.

Preparation.—During the fermentation of grape juice in the production of wine a crude acid potassium tartrate is deposited on the bottom of the vessels used. This substance is termed "argol." On the sides of the tanks a still more impure salt, containing much of the suspended matter of the mixture, is formed as a crust. The "argol" is recrystallised and then forms "tartar," which,

after clarification by means of clay and further crystallisation, is known as "cream of tartar."

Properties.—Potassium bitartrate crystallises in rhombic prisms. 100 parts of water at 15°C. dissolve about 0·5 part of the salt, and at a temperature of 100°C. about 7 parts are dissolved.

When ignited the salt yields a residue of potassium carbonate and carbon.

Tartar is used in very large quantities as an assistant in the mordanting of wool with salts of aluminium, chromium, iron, copper, and tin, and serves to improve the permanence, fulness, and brilliancy of the ultimate colour. This influence is probably due to a double decomposition of the tartrate and the mordanting salt, the mineral acid of the latter combining with the potassium of the tartrate and the metallic hydrate with tartaric acid ; it is also possible that a double salt is formed. At all events it seems that the mordanting salt is changed in such a way that the fibre takes it up more readily and a better result is obtained on dyeing. By mordanting wool with pure tartrates of aluminium, &c., excellent results are obtained. If, moreover, the tartaric acid which has been absorbed by the fibre is not properly washed out, it will, no doubt, exert a less injurious effect in dyeing than sulphuric acid in the free state (*Hummel*). Sometimes, as for instance in mordanting with bichromate and tartar, the latter salt acts also as a reducing agent.

A number of preparations are in the market under the name of *substitute of tartar, tartar cake, superargol,* &c. Some are simply acid sodium sulphate ; others contain oxalates ; while others still consist of tartar, together with sufficient sulphuric acid to convert all the potassium into potassium sulphate. In so far as these preparations claim to replace tartar completely, most of them are useless, because they cannot produce the double decomposition between the mordanting salt and a tartrate. If it is intended to use them for acidifying only, well-known and previously-tested chemicals—such as tartaric or oxalic acid or sodium bisulphate—should be preferred to preparations of unknown composition and properties.

Analysis.—*Acid potassium tartrate* occurring in *cream of tartar, argol,* or *tartar* may be determined in various ways.

Warington, who, with Grosjean, has published many valuable papers on tartaric and citric acids, recommends the following methods for determining the value of commercial tartrates :—

1. (*a*) Five grms. of the finely-powdered sample are heated with a little water and treated with about three-fourths of the total amount of normal caustic required to neutralise it. The liquid is boiled, and when nearly cold, neutralised exactly with a further quantity of normal soda, using phenolphthaleïn as indicator.

$$1 \text{ c.c. of normal alkali} = 0·188 \text{ grm.}$$
$$KHC_4H_4O_6.$$
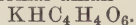
(*b*) Two grms. of the sample are ignited in a platinum crucible at a low red heat. The ash is transferred to a beaker or porcelain basin, and treated with a slight excess of normal sulphuric acid, and the liquid heated to boiling. The excess of acid is then determined by normal alkali. From the alkalinity of the ash of 1 grm. of tartar is subtracted the acidity of 1 grm. of unburnt tartar (both in terms of normal alkali), when the difference represents the neutralising power of the bases existing as *neutral* tartrates. 1 c.c. of normal alkali is in this case equivalent to 0·075 grm. of tartaric acid as neutral tartrate, or 0·113 grm. of $K_2C_4H_4O_6$.

In presence of carbonates, this process does not give the separate amounts of acid and neutral tartrates, but the correct amount of total tartaric acid is obtained.

2. The following process depends upon the conversion of all the tartaric acid present into acid potassium tartrate :—

About 3 grms. of the sample are moistened with a little water, and heated to boiling. The mixture is digested for about twenty minutes with an excess of neutral potassium oxalate, whereby any calcium tartrate is converted into oxalate, with formation of potassium tartrate. From 1 to 2 grms. of potassium oxalate should remain in excess. The liquid is now nearly neutralised with caustic potash, filtered through a small filter, and the residue well washed. The filtrate and washings, containing the whole of the tartaric acid as normal potassium tartrate, are concentrated to about 60 c.c. ; 5 grms. of powdered potassium chloride are added, and the solution allowed to cool. A strong solution of about 3 grms. of citric acid is then added, and the mixture stirred continuously for about ten minutes. The acid potassium tartrate which is thus precipitated is collected on a filter and washed (preferably by the aid of a filter pump) with a 5 per cent. solution of potassium chloride saturated with potassium bitartrate. The precipitate is transferred to the beaker in which the operation was conducted, dissolved in hot water, and titrated with normal alkali, using phenolphthaleïn as indicator.

Each c.c. = 0·150 grm. tartaric acid.

Impurities.—In addition to natural impurities, ground tartar and argol are frequently adulterated with various substances, such as *alum* and *bisulphate of potash*, and occasionally with *gypsum* and *chalk*.

POTASSIUM CARBONATE, K_2CO_3
(*Potashes*).

Preparation. — Carbonate of potash has been known since ancient times as a constituent of the ashes of land plants, from which it is obtained by extraction with water. The extract is evaporated and the residue ignited. It is prepared on the large scale by the Leblanc process from potassium chloride, which occurs in considerable quantity either alone as *Sylvine*, or combined with magnesium chloride as *Carnallite*. It is also obtained from the sulphate, and in smaller quantities from beetroot molasses (vinasse) and "suint."

Properties. — Potassium carbonate is a white solid, which is very hygroscopic and deliquescent. It is readily soluble in water, from which it crystallises as the salt $K_2CO_3 + 1\frac{1}{2}H_2O$. The solution has an alkaline reaction and a caustic taste. If carbon dioxide be passed into the aqueous solution, bicarbonate of potash is formed.

$$K_2CO_3 + CO_2 + H_2O = 2KHCO_3$$
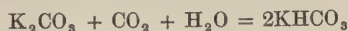
The bicarbonate of potash crystallises from the solution. It is soluble in 3 to 4 parts of water, and has a neutral reaction. On ignition the bicarbonate gives off water and carbon dioxide, the residue consisting of carbonate of potash.

Potassium carbonate is used to a great extent in the manufacture of soft soaps, and of fine glass ware. It is also used in the dyeing of certain direct cotton colours. In most cases sodium carbonate, which it strongly resembles, and which is much cheaper than the potassium salt, can be used in its place.

POTASSIUM CHLORATE, $KClO_3$. *Chlorate of Potash.*

Preparation. — When chlorine is passed through a hot concentrated solution of caustic potash the following reaction takes place :—

$$6KOH + 3Cl_2 = KClO_3 + 5KCl + 3H_2O.$$

A mixture of lime and potassium chloride is used when the manufacture is conducted on a large scale, the calcium chlorate first formed undergoing double decomposition with the potassium chloride.

Potassium chlorate crystallises from the hot solution in shining monoclinic crystals. 100 parts of water dissolve 6 parts of the salt at 15° C., and 60 parts at 100° C.

Properties. — The salt melts at 359°, and on being heated above that temperature gives off oxygen. Potassium chlorate is a powerful oxidising agent. In the presence of sulphur, various sulphides, and organic matter, it is liable to explode, especially if subjected to friction. It is employed in the production of aniline black and manganese bronze, &c., and in the preparation of mordants.

POTASSIUM CHROMATE and BICHROMATE *v.* CHROMIUM TRIOXIDE (CHROMATES).

POTASSIUM FERRICYANIDE, $K_3Fe(CN)_6$. *Red Prussiate of Potash.*—This salt is manufactured by treating the yellow prussiate with oxidising agents such as chlorine :—

$$K_4Fe(CN)_6 + Cl = K_3Fe(CN)_6 + KCl.$$
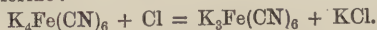
It crystallises in dark red rhombic prisms, which contain no water of crystallisation. 100 parts of cold water dissolve about 35 parts ; hot water dissolve twice as much of the salt. Potassium ferricyanide is an oxidising agent. It is used as a discharge in printing, and in the production of Prussian blue.

POTASSIUM FERROCYANIDE, $K_4Fe(CN)_6 + 3H_2O$. *Yellow Prussiate of Potash.*

Manufacture. — This substance is prepared on the large scale by heating nitrogenous substances, such as leather and horn clippings, wool dust, &c., with scrap iron and crude potashes. The mass is lixiviated, and the aqueous extract crystallised. Large yellow monoclinic crystals containing 3 molecules of water form in the liquid.

Properties.—The crystals lose the whole of their water of crystallisation at 100° C., and form a white powder. Potassium ferrocyanide dissolves in 2 parts of hot and in 4 parts of cold water, the resulting solution having a bitter taste and being non-poisonous. On boiling, the solution evolves ammonia and hydrocyanic acid. On the addition of hydrochloric acid to a concentrated solution of the salt hydroferrocyanic acid, $H_4Fe(CN)_6$, is precipitated as a white powder.

The commercial product generally contains more or less potassium sulphate.

Application. — Potassium ferrocyanide is used in aniline black dyeing and for the production of Prussian blue. It forms precipitates with some basic aniline colours, and can be used as a mordant for these on cotton.

POTASSIUM HYDROXIDE or CAUSTIC POTASH, KOH. *Potassium hydrate.*

Preparation.—When metallic potassium is allowed to act on water, hydrogen is evolved and potassium hydrate is obtained in solution. It is produced on the large scale by boiling 1 part of potassium carbonate dissolved in 12 parts of water with 1 part of slaked lime in an iron vessel.

$$K_2CO_3 + Ca(OH)_2 = 2KOH + CaCO_3.$$
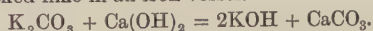
As soon as a filtered sample of the liquid ceases to effervesce (showing complete conversion into hydrate) on the addition of hydrochloric acid, the reaction is at an end. The liquid is decanted, evaporated, and the residue melted and poured into moulds, or broken into lumps.

It is also prepared from potassium sulphate by the Leblanc process, the addition of excess of carbon to the mixture producing a considerable percentage of potassium hydrate.

Properties.—Caustic potash is soluble in alcohol and in half its weight of water. It deliquesces in the air and absorbs carbon dioxide, forming eventually a solution of potassium carbonate.

It is a white crystalline solid having a soapy feel and a strong caustic taste. It is not difficult to melt and is volatilised at a high temperature without change.

Potassium hydrate is the strongest of the bases and possesses marked caustic properties, attacking the skin, paper, &c. It is used in soap-making, &c., but is replaced wherever possible in the arts by sodium hydrate, which is cheaper.

Analysis.—The analysis of caustic potash and potassium carbonate does not differ essentially from that of the corresponding sodium compounds :—

1 c.c. of normal acid = 0·069 grm. K_2CO_3.
,, ,, = 0·056 ,, KOH.
,, ,, = 0·047 ,, K_2O.

Estimation of Potash by Platinum Chloride.—Since potash salts frequently contain considerable quantities of sodium salts, either as natural impurities or adulterations, it is often necessary to estimate the amount of potash present. The alkalimetric process, of course, would include soda, if present. The best method for estimating potassium in presence of sodium salts, although often considered too tedious and expensive for technical purposes, is by precipitation with platinum chloride. Five grms. of the sample are dissolved in 500 c.c. of water. If any insoluble matter be present the liquid can, in the case of potassium carbonate, be run through a dry filter paper ; if a caustic solution, is being tested, it is best to allow the insoluble matter to subside and then draw off 25 c.c. of the clear solution and transfer it to a porcelain dish. A slight excess of hydrochloric acid is added, the dish being meanwhile covered with a clock-glass to prevent loss from effervescence. The clock-glass is removed, taking care to wash the underside into the dish, and an excess of platinum tetrachloride added.

The solution is then evaporated *nearly* to dryness on a water-bath. The liquid should remain dark yellow coloured during the whole of the evaporation, otherwise more platinum chloride must be added.

For further details *v.* ANALYSIS OF AMMONIA.

486 parts of the precipitate (K_2PtCl_6) correspond to 138 parts of K_2CO_3.

If the substance to be analysed contains more than traces of sulphate, the sulphuric acid should be removed by barium chloride, otherwise the potassium platinum chloride is liable to be contaminated with sodium sulphate. This, however, may be prevented without practically affecting the accuracy of the results by having an excess of hydrochloric acid present, and allowing about half a cubic centimetre of liquid to remain in the dish before adding alcohol and ether. During the whole of the process, ammonia fumes should not be allowed to come in contact with the solution, or the results will be too high.

Estimation of Potash by Tartaric Acid.—Two grms. of the sample are washed into a small flask with about 25 c.c. of water, and neutralised by means of tartaric acid. 50 c.c. of a saturated solution of sodium bitartrate are added to the flask, and well shaken at intervals during the course of an hour. The precipitated potassium bitartrate is then collected on a small filter and washed with a cold saturated solution of potassium bitartrate. The filter and contents are put back into the flask, which may contain a little of the precipitate, hot water added, and the solution, with phenolphthaleïn as an indicator, titrated with normal caustic soda.

1 c.c. of $\frac{N}{1}$ soda = 0·069 grm. K_2CO_3, or 0·056 grm. KOH.

Indirect Estimation of Potash and Soda.—From 0·5 to 1 grm. of the sample is dissolved in water and a slight excess of hydrochloric acid is added. The solution is heated to the boiling point and, if any sulphates are present, barium chloride is added. The barium sulphate is removed by filtration, and the excess of barium in solution is precipitated by ammonium carbonate and ammonia. The filtrate from the barium carbonate precipitate is evaporated to dryness in a platinum dish, and the residue ignited to expel ammonium compounds. After cooling, the ignited residue is treated with hot water, and the solution filtered from any insoluble matter. The clear filtrate and washings, with addition of a little hydrochloric acid, are now evaporated to dryness in a weighed platinum dish, and the residue heated to about 180° C. in an air-bath, cooled and weighed. This weight represents the amount of mixed chlorides of potassium and sodium present in the sample, and by estimating the combined chlorine, the amount of potassium and sodium chloride respectively can be calculated. The mixed chlorides are dissolved in water and diluted to 500 c.c. ; 50 c.c. are withdrawn and titrated with $\frac{N}{10}$ silver nitrate, as given under *Analysis of Sodium Carbonate* (*q.v.*). Each c.c. = 0·00355 grm. Cl. The amount of potassium is found by multiplying the difference between the weights of the mixed

chlorides and the chlorine by 1·54, subtracting the chlorine and dividing by 0·63.

POTASSIUM HYPOCHLORITE, KClO. *Eau de Javelle.*—Potassium hypochlorite is known only in aqueous solution, which is obtained by the action of chlorine gas on a cold solution of caustic or carbonate of potash, or by the double decomposition of bleaching powder and potassium carbonate.

$$CaOCl_2 + K_2CO_3 = KClO + KCl + CaCO_3.$$

Eau de Javelle has a chlorine-like smell, and is a strong bleaching agent, the power of which is increased by the addition of an acid (*v.* BLEACHING POWDER, p. 67). It is used chiefly in the household for bleaching purposes.

POTASSIUM MANGANATE *v.* MANGANESE COMPOUNDS.

POTASSIUM METANTIMONIATE *v.* ANTIMONIC ACID.

POTASSIUM NITRATE, KNO₃. *Nitre, Saltpetre.*

Preparation.—Potassium nitrate is found in India as an efflorescence on the soil. It is prepared artificially by allowing waste organic matter containing nitrogen (dung, urine, &c.), to remain mixed with crude potashes and lime in heaps. After standing many months the mass is lixiviated and the calcium nitrate in the extract decomposed by potassium carbonate.

$$Ca(NO_3)_2 + K_2CO_3 = 2KNO_3 + CaCO_3.$$
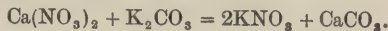
Sodium nitrate can be converted into potassium nitrate by heating saturated solutions of sodium nitrate and potassium chloride together. While hot, sodium chloride crystallises, and, when cold, potassium nitrate separates from the solution.

Properties.—Potassium nitrate crystallises in white rhombic prisms. It is chiefly used in the manufacture of gunpowder. It melts at 338° C., giving off oxygen and forming potassium nitrite (KNO₂).

POTASSIUM NITRITE *v.* POTASSIUM NITRATE.

POTASSIUM OXALATE, K₂C₂O₄ + 2H₂O, is easily soluble in water; it crystallises from aqueous solutions in monoclinic crystals.

Acid Potassium Oxalate, KHC₂O₄, is less soluble in water than the normal salt. It is found in sorrel, rhubarb, and other plants.

Commercial *Salts of sorrel* or *Binoxalate of potash* is a mixture of the two above-mentioned salts. It is used as a substitute for tartar, and sometimes as a mild acidifying substance. It is also employed for removing ink stains.

POTASSIUM PERMANGANATE *v.* MANGANESE OXIDES.

POTASSIUM PERMANGANATE NOR-

MAL SOLUTION *v.* IRON (FERROUS SULPHATE).

POTASSIUM SULPHATE, K₂SO₄, occurs in combination with magnesium sulphate as *Kainite*. It is obtained as a by-product in various industries, and may be prepared by the action of sulphuric acid on potassium chloride. It is used in the preparation of carbonate of potash by the Leblanc process.

POTASSIUM SULPHOCYANIDE or THIOCYANATE, K C N S.—For the preparation of this salt anhydrous potassium ferrocyanide, ignited carbonate of potash, and sulphur are fused together. The mass is lixiviated with water, crystallised and then purified by recrystallisation from alcohol. It crystallises from water and from alcohol in transparent prisms, which deliquesce in the air.

Potassium thiocyanate is very poisonous, and is used in the laboratory as a reagent for ferric salts, with which it gives a red colouration. It may be employed to neutralise those acids which are liable to carry iron into the colours used in calico printing.

POUTET'S REAGENT *v.* OLEIC ACID (COMMERCIAL).

PRAGUE ALIZARIN YELLOW G (Kinzlberger). An azo dye.

Metanitraniline — Beta-resorcilic acid.

1894. Yellow powder, soluble in water. In concentrated H₂SO₄, yellow solution; on dilution, yellow ppt.

Application. — A mordant dye. Dyes chrome-mordanted *wool*, brownish-yellow; chrome-mordanted *cotton*, pure yellow.

PRAGUE ALIZARIN YELLOW R (Kinzlberger). An azo dye.

Paranitraniline — Beta-resorcilic acid.

1894. Orange-yellow powder, soluble in water. In concentrated H₂SO₄, orange-yellow solution; on dilution, orange-yellow ppt.

Application.—*v.* previous colour.

PREPARED BARK *v.* QUERCITRON BARK.

PREPARING SALT *v.* STANNATE OF SODA.

PRIMROSE *v.* EOSINE S.

PRIMROSE SOLUBLE IN ALCOHOL (D. & H.). *Spirit soluble eosin, Methyl eosin* (Mo.) (S. C. I.), *Erythrine.* A phthaleïn derivative. *Potassium salt of tetrabrom fluoresceïn methyl ether.* 1874. Green glistening powder or flakes, slightly soluble in water with a cherry-red colour. In concentrated H₂SO₄, yellow solution, which evolves bromine on heating; on dilution, brownish-yellow ppt.
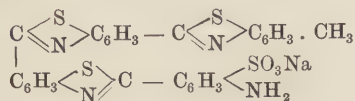
Application.—Dyes *silk* red with brick-red fluorescence.

PRIMROSE *v.* ERYTHROSINE.

PRIMROSE *v.* MARTIUS YELLOW.

PRIMULA *v.* HOFMANN'S VIOLET.

PRIMULINE (Br. S. & Sp.) (By.) (B.) (K.) (C.).　*Carnotine* (Cl. Co.), *Polychromine* (G.), *Thiochromogen* (D.), *Aureolin* (D. & H.), *Sulphin* (B.).　A thiobenzynyl derivative. Mixture of several bodies, the chief of which is—

$$C \underset{N}{\overset{S}{\diagdown}} C_6H_3 - C \underset{N}{\overset{S}{\diagdown}} C_6H_3 \cdot CH_3$$
$$C_6H_3 \underset{N}{\overset{S}{\diagdown}} C - C_6H_3 \underset{NH_2}{\overset{SO_3Na}{\diagdown}}$$

1887.　Dull yellow powder, soluble in water with a yellow colour. In concentrated H_2SO_4, pale yellow solution with green fluorescence; on dilution, orange-yellow ppt.

Application.—A direct cotton colour. Dyes unmordanted *cotton* primrose-yellow from a neutral or alkaline bath. If diazotised and developed on the fibre it produces a series of "ingrain" colours, many of which are very fast.　The chief developers used are the following :—

				Ingrain Cols.
Beta-naphthol,	.	.	.	Red.
Resorcinol,	.	.	.	Orange.
Phenol,	.	.	.	Yellow.
Benzyl naphthylamine,			}	Bordeaux.
Ethyl beta-naphthylamine,				
R salt,	.	.	.	Maroon.
Alpha-naphthol sulphonic acid N W,	.	.	.	Crimson.
Metaphenylene diamine,		.		Brown.

By treating primuline dyed cotton with dilute bleaching powder solution, a very permanent yellow is produced.
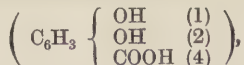
PRINTING BLUE (Ber.) *v* INDULINE SOLUBLE IN SPIRIT.

PRIVET BERRIES contain a small amount of crimson dye, *ligulin*, which may be fixed on alum-mordanted *wool*.

PROOF SPIRIT *v.* ALCOHOL.
PROPIOLIC ACID *v.* INDIGO (ARTIFICIAL).
PROTOCATECHUIC ACID,

$$\left(C_6H_3 \left\{ \begin{array}{ll} OH & (1) \\ OH & (2) \\ COOH & (4) \end{array} \right. \right),$$

is produced by fusing catechu and many other vegetable principles with caustic potash. It may also be readily obtained by synthesis. It forms monoclinic needles, melting at 199° C., and its aqueous solution gives with ferric salts a bluish-green coloration, which changes to a deep red on neutralising with sodium carbonate.　By distillation of its calcium salt *catechol* (pyrocatechin) is formed.

PRUNE PURE (Sandoz).　*Parma R* (Sandoz). An oxazine dye. *Dimethyl phenyl-ammonium dioxyphenoxazine carboxylic acid methylether.*　1886. Brown glistening crystals or dark brown powder or paste, slightly soluble in water. In concentrated H_2SO_4,

cornflower blue solution, which changes to magenta-red on dilution.

Application.—A basic and a mordant dye. Dyes tannin-mordanted *cotton* or chrome-mordanted *cotton* or *wool* blue-violet.

PRUSSIAN BLUE.—By the reaction of ferrous and ferric salts with yellow and red prussiate of potash, several compounds are produced.

Yellow prussiate and ferrous salts produce together a white compound, which oxidises rapidly to form Prussian blue. The white compound probably has the composition $K_4Fe_2(CN)_{12}Fe_2$. Ferric salts produce in a solution of yellow prussiate, when the latter is in excess, a blue precipitate of *ferric potassium ferrocyanide*, $K_2Fe_2(CN)_{12}Fe_2$. This substance, usually called *soluble Prussian blue*, dissolves, when pure, in water forming a blue solution, from which it is precipitated by the addition of salts.

Preparation.—70 parts of ferrous sulphate crystals are dissolved in water, and the hot solution is gradually added to a boiling solution of 110 pats of potassium ferricyanide. The mixture is boiled for two hours, filtered, and washed with water. When the washings which pass through begin to assume a deep blue colour the washing must cease.

Molybdic acid and ammonium molybdate and tungstate easily dissolve Prussian blue.

Turnbull's blue or *ferrous ferricyanide*, $Fe_5(CN)_{12}$, or $(Fe_2)_2(Fe_2)_3(CN)_{24}$, is formed by precipitating ferrous sulphate with red prussiate. *Williamson's blue* or *insoluble Prussian blue*, or *ferric ferrocyanide*, $Fe_7(CN)_{18}$, or $(Fe_2)_4(Fe_2)_3(CN)_{36}$, is obtained, together with soluble Prussian blue, when a solution of yellow prussiate is added to a solution of ferric chloride.　The same compound is obtained by the action of chlorine or nitric acid on Turnbull's blue, or by precipitating the soluble Prussian blue with ferric chloride. The *pigment Prussian blue* is prepared by precipitating a solution of copperas with yellow prussiate of potash, and oxidising the white product with nitric acid. It forms an intensely blue powder or lumps having a coppery lustre, and consists of mixtures of the various blues. It is quite insoluble in water, but dissolves in ammonium tartrate with a violet, and in oxalic acid with a blue, colour.　It is insoluble in mineral acids and is not affected by them, but it is decomposed by alkalies with formation of ferric hydroxide and ferrocyanide ; for instance :—

$$2Fe_7(CN)_{18} + 24KOH$$
$$= 3K_8(CN)_{12}Fe_2 + 4Fe_2(OH)_6.$$
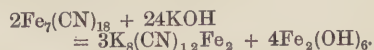
Hydroferrocyanic acid, $H_8(CN_{12})Fe_2$ (or an acidulated solution of yellow prussiate), is dissociated on boiling ; hydrocyanic acid escapes, while a white precipitate of an acid ferrous ferrocyanide is formed,

$$2H_8(CN)_{12}Fe_2 = 12HCN + H_4Fe_2(CN)_{12}Fe_2.$$

The same reaction is used for the preparation of hydrocyanic acid.

If an oxidising agent is present—*e.g.*, red prussiate—the reaction is somewhat different, and Williamson's blue is formed, together with hydrocyanic acid,

$$7H_8(CN)_{12}Fe_2 + 2O_2$$
$$= 2Fe_7(CN)_{18} + 48HCN + 4H_2O.$$
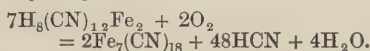
Use is made of this reaction for the production of Prussian blue in wool dyeing and in calico printing. In the latter case a mixture of yellow and red prussiate and tartaric acid is printed on the material, and then steamed. Prussian blue may be considered to be a mordant colour produced by the dyestuff "yellow prussiate," combined with ferric mordant. The colour deserves to be called polygenetic, since the prussiates produce various coloured products with most of the metallic oxides. Prussian blue, however, is the only one of the series which is used in dyeing, printing, or painting.

PUCE SPIRIT *v.* TIN SPIRITS.

PURE BLUE *v.* SOLUBLE BLUE.

PURE BLUE B S I (S.C.I.) *v.* BAVARIAN BLUE D B F.

PURPLE SPIRITS *v.* TIN SPIRITS.

PURPLE TREFOIL (*Trifolium pratense purpureum*) contains a bright yellow colour, which is used in staining wood.

PURPURIN (NATURAL) *v.* MADDER.

PURPURIN. Old name for ROSOLANE.

PURPURIN (B.) (By.) (Brit. Aliz. Co.). *Alizarin No. 6* (M.). An anthracene derivative, isomeric with *anthra-* and *flavo-purpurin* and anthracene brown. *Trihydroxy anthraquinone*. Exists naturally in Madder root in small quantities. Prepared from madder in 1826, from anthracene in 1874. Reddish-brown paste, slightly soluble in water. In concentrated H_2SO_4, reddish-yellow solution; on dilution, reddish-brown ppt. In caustic alkali solution, magenta colour.
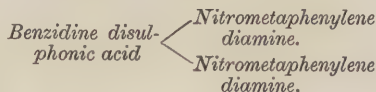
Application.—*v.* ALIZARIN.

PURREE *v.* INDIAN YELLOW.

PYOKTANIUM or PYOKTANINE. Methyl violet is sold as an antiseptic under this name.

PYRENE *v.* ANTHRACENE.

PYRAMINE ORANGE (B.). An azo dye.

Benzidine disulphonic acid
⎰ Nitrometaphenylene diamine.
⎱ Nitrometaphenylene diamine.

1893. Reddish powder, giving an orange-red solution in water. In concentrated H_2SO_4, yellow solution; on dilution, yellow-red ppt.

Application.—A direct cotton colour. Dyes *cotton* orange-red from a neutral or alkaline bath.

PYROGALLIC ACID. (*Pyrogallol. Trihydroxybenzene*).

$$\left(C_6H_3 \left\{ \begin{array}{l} OH\ (1) \\ OH\ (2) \\ OH\ (3) \end{array} \right. \right).$$
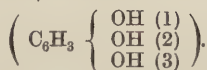
This body is formed by the dry distillation at a low temperature of tannic or gallic acid, or of any of those tannin matters which produce "bloom" on leather or give a blue colour with ferric salts. It may also be produced synthetically. It forms colourless needles, which melt at 131° C., and is volatile at a slightly higher temperature. It dissolves easily in water, alcohol, or ether, its solutions being poisonous. In alkaline solution it has a very powerful reducing action, and is used on this account in photography, and as an oxygen absorber in gas analysis.

The production of *pyrogallol* or *catechol* respectively, when a tannin is submitted to dry distillation, is employed as a means of classifying these substances. The details of the method of carrying out the test are as follows :—*1 grm. of the tannin is dissolved in 5 c.c. glycerine and the solution heated slowly to 160° C. After ten minutes the temperature is raised to 200° C., and kept between 200° and 210° for half an hour. It is then allowed to cool, and the liquid shaken with 50 c.c. of ether. The separated ethereal layer is evaporated to dryness, the residue dissolved in 50 c.c. of water and tested for pyrogallol and catechol by means of the following table :—

	Pyrogallol.	Catechol.
Ferric chloride, .	Red colour, turning brown.	Green colour.
Ferric acetate, .	Dark purple colour.	Green colour.
Lime water,. . .	Purple colour, turning brown.	Red colour.
Melting point,. .	131°	111°
Pinewood shaving, moistened with HCl, ...	No change.	Violet colour.

Pyrogallol is largely employed in colour making, chiefly for the production of "alizarin" or "anthracene" yellows.

PYROLIGNEOUS ACID *v.* ACETIC ACID.

PYROLIGNITE OF IRON *v.* IRON (FERROUS ACETATE).

PYROLUSITE *v.* MANGANESE.

PYRONINE B (L.) (By.). A derivative of diphenylmethane. *Tetra ethyl diamido oxydiphenylmethane hydrochloride.* 1889. Green glistening crystals, soluble in water with a red colour with yellowish-red fluorescence. In concentrated H_2SO_4, yellowish-red solution, which becomes redder on dilution.

* Trimble, *The Tannins*, vol. i., p. 27.

Application.—A basic colour. Dyes tannin-mordanted *cotton* bluish-crimson.

PYRONINE G (L.) (By.). The corresponding tetramethyl derivative.

The *Appearance, Reactions,* and *Properties* are similar to those of PYRONINE B, but its aqueous solution has a yellow fluorescence, and it dyes a redder shade.

PYROSINE B (Mo.) *v.* ERYTHROSINE.

PYROSINE J (Mo.) *v.* ERYTHROSINE G.

PYROSINE R (Mo.). A mixture of *B* and *J.*

PYROTINE ORANGE (D.) *v.* CROCEÏN ORANGE.

PYROTINE RED RRO (D.). An azo dye.

Beta-naphthylamine   *Alpha-naphthol*
monosulphonic — *monosulphonic*
acid D   *acid N W.*

1884. Brownish-red powder, giving a yellowish-red solution in water. In concentrated H_2SO_4, magenta-red solution, which becomes redder on dilution.

Application.—An acid colour. Dyes *wool* and *silk* red from an acid bath.

PYROXYLIN *v.* ARTIFICIAL SILK ; also COTTON (ACTION OF HNO_3 ON CELLULOSE).

Q

QUERCETIN *v.* QUERCITRON BARK ; also PERSIAN BERRIES.

QUERCITANNIC ACIDS are the tannins existing in various species of oak bark, and although they are all probably identical, this fact is not yet established. The composition has been given as $C_{19}H_{16}O_{17}$, and in the pure condition they form a pinkish-white amorphous powder, soluble in water or alcohol, but insoluble in ether. Quercitannic acids give a blue-black coloration, or precipitate with ferric salts, and a dirty white precipitate with tartar emetic. They also form compounds with albumen and gelatine, and are the most important tannins used in the production of leather. They are very little used in dyeing.

QUERCITRIN *v.* QUERCITRON BARK.

QUERCITRON BARK and FLAVIN.

Origin.—Quercitron is the inner bark of the *Quercus nigra* or *Q. tinctoria,* a species of oak indigenous to the United States and Central America. It was first introduced into this country by Bancroft in 1775 as a cheap substitute for weld.

The bark of the tree may be divided into three layers, viz. :—A black, coarse, outer bark, which contains little colouring matter, and is discarded ; a central cellular portion, in which the colouring matter chiefly resides ; and an inner woody bark. In preparing the dyestuff the rough outer bark is chopped off, and the central portion, when rasped, constitutes the commercial article.

The colouring matter is found chiefly in the powdery substance, which may be sieved away from the rasped bark.

Commercial Preparations.—In addition to "bark extract," which is prepared in the usual way (*v.* Logwood extract), this colouring matter is sold in three forms, viz., "flavin," "patent bark," and "prepared bark."

Prepared bark is little used, and appears to be ordinary rasped bark, from which a good deal of the fibrous portion has been removed by sifting or other means.

Patent bark is prepared by boiling ground quercitron bark with dilute sulphuric acid, and then washing and drying the product. The process thus consists essentially in the decomposition of the glucoside contained in the bark. Patent bark has about double the dyeing power of the rasped bark.

Flavin is the most important product of the series, being, indeed, more largely used than quercitron bark itself. Two distinct processes are in use for its preparation. In the older method the ground bark is extracted with superheated water, from which flavin precipitates on cooling. Prepared in this manner, flavin consists of impure *quercitrin* (see below), while the more esteemed kinds of flavin consist essentially of *quercetin.* These are prepared by carefully extracting the bark powder ("prepared bark") with ammonia, or other alkali, and then immediately acidifying the solution in order to prevent the oxidation which readily occurs when the colouring matter in alkaline solution is exposed to the air.

COLOURING MATTER OF QUERCITRON BARK.

As in the case of weld and many other dyestuffs, the colouring principle of quercitron bark was first isolated by Chevreul, who named it *quercitrin.* He also obtained from the bark a peculiar tannin, *quercitannic acid.* Quercitrin may be prepared as follows:—The ground bark is extracted with alcohol, and to the concentrated extract a considerable amount of glacial acetic acid is added. An alcoholic solution of lead acetate is then carefully added to precipitate the impurities, crude quercitrin being obtained from the filtrate by evaporating to dryness after removing the lead by means of hydrogen sulphide. The product is then purified by dissolving in alcohol, re-precipitating with water, and re-crystallising several times from hot water after filtering through animal charcoal.

Quercitrin, when pure, crystallises in pale yellow needles. It is insoluble in cold, but slightly soluble in boiling water, and easily soluble in alcohol, acetic acid, or alkalies. The percentage composition of *quercitrin* is not well established, Rochleder giving the formula $C_{33}H_{30}O_{17}$, while Liebermann and Hamburger's analytical results require $C_{36}H_{38}O_{20}$. It appears to be a glucoside, being

decomposed by boiling with dilute mineral acid with production of a flocculent precipitate of *quercetin ;* a sugary substance (*isodulcitol* or *rhamnose*) remaining in solution.

With ferric chloride quercitrin produces an intense green coloration. It possesses a certain dyeing power, but is much inferior to quercetin in this respect.

Quercetin, the true colouring matter of quercitron bark, is most readily prepared in the following manner * :—Quercitron bark dust is washed with salt solution to remove impurities, and then extracted with cold dilute ammonia. The extract, on neutralisation with sulphuric acid, deposits a brown precipitate containing little colouring matter. This is filtered off, and the clear solution is acidified and boiled. Crystals of quercetin soon begin to separate, and are collected from the hot liquid, in order to prevent contamination with impurities which are deposited on cooling. If necessary, it is recrystallised from alcohol.

When pure, quercetin crystallises in yellow needles. Of the several formulæ which have been assigned to it, A. G. Perkin † has recently shown that of Herzig ‡ ($C_{15}H_{10}O_7$) to be correct. Quercetin is insoluble in cold, but slightly soluble in hot water, and readily soluble in alcohol or alkaline solutions. With ferric chloride it gives a similar dark green solution to that produced by quercitrin, but the former becomes red, and the latter is unchanged on heating.

Quercetin gives interesting decomposition products when fused with solid caustic potash, § including *paradatiscetin, quercetic acid, phloroglucin,* and *proto-catechuic* acid.

Under suitable conditions it forms halogen and alkyl derivatives, and behaves in a similar manner to *morin* (old fustic) and *fisetin* (young fustic) when acted upon by strong mineral acids. ‖

Quercitrin and quercetin exist not only in quercitron bark, but in a large number of plants.

Application.—Flavin is used in conjunction with tin mordant for the production of bright orange-yellow shades of wool. A small addition of flavin is frequently made when dyeing cochineal scarlets. This removes the somewhat bluish tone of the cochineal, and produces a more brilliant scarlet.

Bark extract is employed in *calico* printing for producing yellows with alum and tin mordant.

QUICKLIME *v.* Calcium Oxide.

QUINOLINE or CHINOLINE, C_9H_7N. Quinoline is one of a homologous series of bases obtained from coal-tar naphtha, which

* A. G. Perkin, *J. Chem. Soc. Trans.*, 1895, p. 646.
† *Journ. Chem. Soc. Trans.*, 1895, p. 648.
‡ Monatsch, 1891, p. 172.
§ *Dict. of Applied Chem.*, Thorpe, vol. iii., p. 324.
‖ A. G. Perkin, *J. Chem. Soc. Trans.*, 1895, p. 652.

distil over after the pyridine bases (above 200° C.). The quinoline bases are also produced by the distillation of chinoline, cinchonine, &c., with potassium hydrate. These basic substances are oily liquids, insoluble in water, but easily soluble in alcohol and ether.

Quinoline may be made artificially by heating together nitrobenzene, glycerin, aniline, and sulphuric acid. After distilling off the excess of nitrobenzol, caustic soda is added to the residue, and the quinoline is distilled off in a current of steam.

Quinoline is a strongly refractive liquid, having a specific gravity of 1·081 at 0° C., and boiling at 235° C. It is used in the manufacture of certain colouring matters.

QUINOLINE BLUE (G.). *Cyanine.* A quinoline derivative, obtained by the action of *amyliodide* upon a mixture of *quinoline* and *lepidine,* and treatment of the product with *caustic soda.* 1856. Glistening green crystals, slightly soluble in water with a violet-blue colour. In concentrated H_2SO_4, colourless solution, which evolves iodine on heating ; no change on dilution.

Application.—Employed for rendering photographic plates orthochromatic.

QUINOLINE RED (Ber.). A quinoline derivative, obtained by the action of *benzotrichloride* on a mixture of *izoquinoline* and *quinaldine* in presence of a dehydrating agent. 1882. Dark brownish-red bronzy crystals, slightly soluble in water, easily in alcohol. In concentrated H_2SO_4, colourless solution, which becomes red on dilution.

Application.—*v.* Quinoline Blue. A mixture of the two is sold as *Azalin.*

QUINOLINE YELLOW SOLUBLE IN SPIRIT (Ber.) (By.) (B.). *Quinophthalone.* A quinoline derivative, obtained by heating *quinaldine* with *phthalic anhydride* in presence of a dehydrating agent. 1882. Yellow, insoluble powder. In concentrated H_2SO_4, yellowish-red solution ; on dilution, yellow ppt.

Application.—Used in colouring spirit varnishes, soaps, &c.

QUINOLINE YELLOW SOLUBLE IN WATER (Ber.) (By.) (B.). *Sodium salt of the disulphonic acid* of the above. 1882. Yellow soluble powder. In concentrated H_2SO_4, yellowish-red solution ; on dilution, yellow solution.

Application.—An acid colour. Dyes *wool* and *silk* greenish-yellow from an acid bath.

QUINOPHTHALONE *v.* Quinoline Yellow Soluble in Spirit.

R

RAMIE *v.* China Grass.
RAURACIENNE *v.* Fast Red A.
RECTIFIED SPIRITS OF WINE *v.* Alcohol.
RED B (B.) (F.) *v.* Sudan II (Ber.).

RED C (B.) v. Sudan III (Ber.).
RED CORALLINE v. Coralline.
RED COTTON SPIRITS v. Tin Spirits.
RED EXTRACT OF INDIGO v. Indigo.
RED LEAD v. Lead Tetroxide.
RED LIQUOR v. Aluminium Acetates.
RED M (Mo.). An azo dye.

Benzidine $\Big\langle$ *Meta-amidophenol.*
Naphthionic acid.

1891. Dark red powder, almost insoluble in water. In concentrated H_2SO_4, blue solution, which becomes colourless on dilution.
Application.—A direct cotton red.
RED OIL v. Oleic Acid (Commercial).
RED PRUSSIATE OF POTASH v. Potassium Ferricyanide.
RED SANDERS v. Sanderswood.
REDUCED INDIGO v. Indigo.
RED VIOLET 4 R S (B.). *Acid violet 4 R S* (M.). A rosaniline derivative. *Sodium salt of dimethyl rosaniline trisulphonic acid.* 1877. Reddish-violet powder, soluble in water with a magenta colour. Alcoholic solution, reddish-violet. In concentrated H_2SO_4, brownish-yellow solution, which changes to magenta-red on dilution.
Application.—An acid colour. Dyes *wool* and *silk* from an acid bath a somewhat bluer shade than acid magenta.
RED VIOLET 5 R EXTRA (B.) v. Hofmann's Violet.
RED VIOLET 5 R S (B.). A rosaniline derivative. *Sodium salt of ethyl rosaniline trisulphonic acid.* 1877. Brownish-violet metallic glistening lumps, soluble in water with a magenta colour. Alcoholic solution, reddish-violet. In concentrated H_2SO_4, yellow solution, becoming magenta-red on dilution.
Application.—An acid colour. Dyes *wool* and *silk* bluish-red from an acid bath.
REDWOODS. The red dyewoods are divisible into two classes, distinguished as "*soluble*" and "*insoluble*" redwoods, so called because the colouring matters of the former are easily soluble in water, while those of the latter are not.

INSOLUBLE REDWOODS.

This class of dyewoods is characterised by the great insolubility of their colouring matters, and are sometimes designated as the "close" or "hard" redwoods. The class includes *Camwood, Barwood,* and *Sanderswood,* and the less generally known *Caliaturwood* and *Madagascar-wood. Mahogany* is very closely allied.

These woods are all very hard and resinous, and of a high specific gravity. On account of their rich colour and general properties, they are well adapted for cabinet work—mahogany, the most quickly grown, being most esteemed for this purpose. For the use of the dyer the wood from old trees is best, since it contains the most colouring matter.

Commercial Preparations.—The insoluble redwoods, generally speaking, undergo no preparatory process, save that of grinding, before being used by the dyer. It is, however, the practice in this country to submit camwood to the "ageing" process; but this is not considered necessary, and is usually omitted in the case of barwood and sanderswood. On account of the insolubility of the colouring matters of this class of dyewoods, it is not possible to prepare extracts in the same way as is done with logwood and Brazilwood, and practically the ground wood is always employed.

A. Zandu proposed to make a soluble sulphonated extract, analogous to indigo extract, by treating the resinous colouring matter, obtained by extracting the wood with alcohol, with concentrated sulphuric acid, but the process does not appear to have any practical importance.

Barwood is the wood of *Baphia nitida,* a large tree growing freely in Sierra Leone and Angola. It is similar in appearance and character to sanderswood, but its aqueous solution is devoid of smell.

Caliatur or Cariatur wood appears to be a variety of sanderswood, having the same aromatic smell, and being otherwise very similar. It is exported from the East Indies, and is used principally in Germany and France.

Camwood or Kambewood is botanically apparently closely allied to barwood, some stating that it is produced by a variety of *Baphia nitida,* but this is uncertain. It is imported from the Gaboon and Congo basins, Sierra Leone, &c., and was first brought to Europe by the Portuguese, by whom it was called Pas-gaban (Gaboon wood).

Camwood is considerably richer in colouring matter than either sanderswood or barwood. It produces bluer shades, and the colouring matter is more easily soluble in water.

Sanderswood, also called *Santal, Sandal,* or *Red Sanders,* is obtained from the *Pterocarpus santalinus.* It is imported from the East Indies, Ceylon, the coasts of Coromandel and Malabar, Golconda, Madagascar, and tropical Africa generally. It is shipped in the form of hard compact billets of a dull red colour, and is subsequently ground or rasped to coarse powder. When boiled with water it gives off an aromatic odour resembling that of orris root.

Colouring Matters of Insoluble Redwoods.

The chemistry of the insoluble redwoods has not been much investigated, and it is not

known whether they all contain the same colouring matter. If not identical, they are, however, probably very closely allied.

Sanderswood has been the most studied, the colouring matter being first isolated by Pelletier in the form of a red resin, by the evaporation of an alcoholic extract. To this product the name *Santal red* has been given, and it may be obtained in a purer form by extracting sanderswood with ether, and evaporating the solution to crystallisation. The crystalline mass is then boiled with water to remove the impurities, and after dissolving in alcohol, is precipitated with alcoholic lead acetate solution. After washing, the lead salt is decomposed by sulphuric acid in alcohol, filtered, and the alcoholic solution of the colouring matter allowed to crystallise.

This process, due to Meier, yields the colouring matter in the form of minute red crystals, the pure product being known as *Santalin* or *Santalic acid*. It is insoluble in cold, but slightly soluble in boiling, water. It dissolves in alcohol with a red, and in ether with a yellow, colour, and is also soluble in acetic acid (sparingly), and alkalies (easily). Its melting point is 104° C., and its composition has been variously given as $C_{16}H_{16}O_3$ (Pelletier *) and $C_{15}H_{14}O_5$ (Weyermann and Haffely†). According to Meier, sanderswood contains six distinct extractive matters, four of which are soluble and two insoluble in water—the latter being *Santalin*, and *Santal*, a colourless, crystalline body of the composition $2C_8H_6O_3 3H_2O$. Alkaline solutions of *Santal* have a yellow colour, which becomes rapidly red on exposure to air, owing to the absorption of oxygen and production of *Santalin*. Santal is, therefore, considered to be reduced santalin.

Weidel has corroborated Meier's results in respect to these two substances, but there appears to be some doubt as to the individuality of the four soluble substances above mentioned.

Weidel also obtained a scarlet crystalline product by extracting sanderswood with alkali, then drying it and extracting with ether. To this he assigned the formula $C_{14}H_{12}O_4$, but was unable to obtain anthracene from it by reduction with zinc dust. When fused with caustic alkali, santal yields

proto-catechuic acid $C_6H_3{<}^{(OH)_2}_{COOH}$.

Cazeneuve and Hugounenq have obtained two additional crystalline substances from sanderswood — viz., *Pterocarpin* ($C_{20}H_{16}O_6$) and *Homopterocarpin* ($C_{21}H_{24}O_6$), the latter of which, these investigators think, may be a polymerised form of orcin ($C_7H_8O_2$), the chromophor of orchil and cudbear.

* *Journ. de Pharmacie et de Chimie*, vol. lxxix., p. 258.
† Liebig's *Annalen der Chemie*, lxxiv., p. 226.

Anderson has isolated from barwood *Baphic acid* and *Baphin*, which may possibly be identical with *Santal* and *Santalin* respectively. Anderson states that barwood contains at least three colouring matters in addition to these.

The colouring matters of camwood have not been investigated.

Application of Insoluble Redwoods. — On account of the insolubility of the colouring matters of these dyewoods there is, at any given moment, only a very small amount in solution in the dye-bath, and as this is absorbed by the wool a further small portion dissolves out, the process of solution and absorption being continuous but slow. To exhaust the dye it is necessary to boil for at least one and a-half to two hours; and the injurious action of this long boiling upon the wool fibre appears to be intensified by some specific action of the dye itself, wool being invariably rotted to some extent when dyed with these woods.

In all cases, when dyeing with the insoluble redwoods, the fullest colours are obtained by using the "stuffing and saddening" process —*i.e.*, by boiling first with the dyestuff and afterwards with the mordant. The insoluble redwoods are chiefly used in conjunction with logwood, fustic, madder, &c., for the production of browns, drabs, olives, &c., on wool. Sumach is also frequently added, but this is only rational where iron mordant is employed, in which case the grey tannate of iron which is produced aids in darkening the colour.

Camwood has at least double the dyeing power of other woods of this class.

Tests for Insoluble Redwoods.—Wool dyed with insoluble redwoods, in conjunction with mordants, does not give up any colour on boiling with water or dilute alkali, but with dilute mineral acid a red coloured solution is obtained from which alkali precipitates the colour-lake. *Chlorine* gas quickly bleaches the colours. *Alkalies* render them bluer in shade; acids redden them.

SOLUBLE REDWOODS.

Origin.—This group includes several closely allied dyestuffs, all of which are produced by trees belonging to the natural order *Leguminosæ*, Genus, *Cæsalpinia*. The distinction between the various species is not well defined, but the following are fairly well characterised, although frequently sold indiscriminately under the name "Brazilwood" or "peachwood":—

(1) Brazilwood (*Cæsalpinia Braziliensis*) is imported from Brazil, in the form of hard irregularly-shaped blocks, having externally a dark brownish-red colour. The central portion of the logs, which has not been

exposed to the action of the atmosphere, is pale yellow.

The use of Brazilwood as a dyestuff is of great antiquity, antedating considerably the discovery of South America ; in fact, from apparently conclusive data, Bancroft states that the name " Brazil " was given to the country on account of the extensive forests of the already well known " Brazilwood," which were found by its Portuguese discoverers. The dyestuff thus gave its name to the country from which it was afterwards principally obtained, and it is not the case, as is generally supposed, that it owes its name to the country of its origin, as do many other dyestuffs.

The word " Brazil" appears to have been originally used to designate a bright red or flame colour. Thus, in a contract between the cities of Bologna and Ferrara in 1194, the dyestuff *Kermes* is referred to as *grana de brazile*, and *Brazilwood* (probably sapanwood) is also mentioned, both dyestuffs at that time being obtained from India.

Brazilwood proper is not now exported to any considerable extent, the forests within easy reach of the coasts having become exhausted. Several of the other varieties are also much richer in colouring matter.

(2) Pernambuco (sometimes Fernambuco) wood (*Cæsalpinia crista*) is a variety of Brazilwood imported from Pernambuco, Paraiba, and Jamaica. It is poor in colouring matter.

(3) Sapanwood (*Cæsalpinia sappan*) is indigenous to India, Ceylon, Siam, East Indies, Japan, and Persia, and was the variety of Brazilwood first employed in Europe. It varies much in quality, " Siam " and " Bangkok " being the most esteemed varieties, while " Manila " is quoted at a considerably lower price.

(4) Nicaragua, peach, or Saint Martha wood (*Cæsalpinia echinata*) is imported from various Mexican ports, and good qualities are very rich in colouring matter.

(5) Limawood is frequently considered as a variety of sapanwood, but is more probably a distinct species of *Cæsalpinia*. It is imported from Tehuantepec, Pera, Altata, and Manzanilla, and the last-named variety of Limawood is the strongest dyestuff in the group of soluble redwoods.

(6) Jamaica wood (*Cæsalpinia vesicaria*), along with woods from California, Sierra Firma, and Bahia, is usually sold as one or other of the above-named varieties.

Commercial Preparations.

All the soluble redwoods are imported in the form of small logs, and are ground by the dyewood cutter into a coarse powder. This is then submitted to the "ageing" process, or used for preparing extracts, in exactly the same way as logwood, and the efficacy of the ageing process is probably due to the same cause as in the case of logwood (*q.v.*). The extracts are sold either as " *sapan liquor* " at 5° to 12° Tw., or " *Brazil extract* " at 20° to 50° Tw.

Beautifully coloured lakes, which are used for painting and paper staining, are also prepared from the soluble redwoods. " *Florence* " or " *Berlin lake* " is obtained by saturating an aqueous decoction of the wood with a mixture of chalk, alum, and starch, while the somewhat brighter " *Venetian* " lake is produced by precipitating with gelatinous alumina and gelatine, then adding a little alum, drying, and grinding. A bluer shade is obtained by adding a little alkali (soap or borax) before drying.

Colouring Matter in Soluble Redwoods.

The woods all appear to contain the same colouring matter. In the freshly-cut wood it exists as a colourless colouring principle, *brazilin*, which, by oxidation, is converted into the true colouring matter, *brazilein*— these substances closely corresponding to the *hæmatoxylin* and *hæmatein* found in logwood.

Brazilin forms yellow rhombic prisms, which when crystallised from alcohol have the composition $C_{16}H_{14}O_5H_2O$. From water it crystallises as $2C_{16}H_{14}O_5 \cdot 3H_2O$. It is easily soluble in alcohol, ether, or hot water. Several of the reactions of *brazilin* indicate that it is a derivative of an aromatic hydrocarbon.

When treated with nitric acid it yields *trinitro resorcinol* $\left(C_6H\!<\!\genfrac{}{}{0pt}{}{(OH)_2}{(NO_2)_3} \right)$, and when submitted to dry distillation, or when fused with caustic alkali, *resorcinol* $(C_6H_4 \cdot (OH)_2)$ is obtained. Again when treated with powerful reducing agents, it yields first *brazinol* $(C_{16}H_{14}O_4)$, and finally a hydrocarbon $(C_{16}H_{14}?)$.

Brazilein, the true colouring matter, has the composition $C_{16}H_{12}O_5$. It may be prepared by aspirating a gentle current of air for a few hours through an aqueous solution of brazilin rendered slightly alkaline with ammonia, then acidifying with acetic acid, and crystallising the brown amorphous precipitate thus obtained from dilute acetic acid. Prepared in this manner brazilein forms a dark brown, almost black crystalline mass, with a steel grey metallic lustre.

Brazilein is soluble, but not easily so, in hot water, alcohol, or ether, with a brownish-yellow colour. It readily gives a crimson-red solution in alkalies, which solution quickly absorbs oxygen, and is converted into brown products ; and in this, as in many other reactions, brazilein and hæmatein, the colouring

matter of logwood, show a great similarity in behaviour, which is probably to be explained by a similarity in constitution.

When brazilein is dissolved in concentrated sulphuric acid, and the solution diluted with a large volume of water, a new body of the composition $C_{16}H_{11}O_5HSO_4$ is precipitated. The corresponding chloride, $C_{16}H_{11}O_5Cl$, is produced by heating brazilein with hydrochloric acid to 100° C. in a sealed tube.

COMPARISON OF THE SOLUBLE REDWOODS.

The amount of colouring matter contained in the different species of *Cæsalpinia* varies greatly. Taking an average quality of each wood, *limawood* and *peachwood* are considerably richer than other varieties—the latter giving, as a rule, somewhat the brighter shades of the two. The other members of the group — *Brazilwood, Pernambuco,* and *sapanwood*—give paler colours; but the true *Brazilwood*, from *C. Braziliensis*, is remarkable for brilliancy of colour.

APPLICATION OF SOLUBLE REDWOODS.

Latterly, the use of these dyestuffs has greatly decreased, although the fact that some 2000 tons are still annually imported into the United Kingdom shows that they are by no means obsolete.

The soluble redwoods give bright crimson shades on wool or silk previously mordanted with alum, and deep purple shades with chrome mordant.

Brazil extract is used in calico printing.

REGINA PURPLE (Br. S. & Sp.). *Regina violet* (Br. S. & Sp.), *Imperial violet, Phenyl violet*. A rosaniline derivative. *Acetate of monophenyl or monotolyl rosaniline and pararosaniline*. 1860. Green powder, soluble in water with a reddish-violet colour. Alcoholic solution, bluish - purple. In concentrated H_2SO_4, brown solution; unchanged on dilution.

Application.—A basic colour. Dyes *wool* reddish-violet from a neutral bath.

REGINA VIOLET SOLUBLE IN SPIRIT (Ber.). A rosaniline derivative. *Hydrochloride of diphenyl rosaniline*. Obtained as a by-product in the manufacture of magenta by the nitro-benzene process. Green powder, slightly soluble in water with a violet colour; easily soluble in alcohol with a bluish - purple colour. In concentrated H_2SO_4, brown solution; on dilution, brown ppt.

Application.—A basic colour. Used only in *silk* dyeing.

REGINA VIOLET SOLUBLE IN WATER (Ber.). The trisulphonic acid of the preceding. Bronzy lumps or powder, soluble in water with a violet colour. In concentrated H_2SO_4,

it produces a deep brown solution which, on dilution, becomes violet.

Application —An acid colour. Dyes *wool* reddish-violet from an acid bath.

RESIN *v.* SOAP.

RESORCIN BLUE *v.* FLUORESCENT BLUE.

RESORCIN BROWN (Ber.). An azo dye.

$$Resorcin \begin{cases} Metaxylidine. \\ Sulphanilic \ acid. \end{cases}$$

1881. Brown powder, soluble in water. Alcoholic solution, yellowish-brown. In concentrated H_2SO_4, brown solution; on dilution, brown ppt.

Application.—An acid colour. Dyes *wool* brown from an acid bath.

RESORCIN BROWN (H.). 1888. An acid-mordant dye, producing reddish-brown shades on wool in an acid bath, which become much darker by subsequent treatment with bichromate of potash.

RESORCIN YELLOW (Ber.) (K.) (Fi.). *Chrysoin* (P.) (B.) (D. & H.) (G.) (M.), *Chryseolin yellow T* (S.C.I.), *Acme yellow* (L.), *Gold yellow* (By.), *Acid yellow RS* (D.), *Tropæolin O* (R.) (C.). An azo dye.

Sulphanilic acid — Resorcinol.

1875. Brown powder, soluble in water with a reddish-yellow colour. Alcoholic solution, bright yellow. In concentrated H_2SO_4, yellow solution, becoming reddish - yellow on dilution.

Application.—An acid dye. Dyes *wool* and *silk* reddish-yellow from an acid bath.

RETTING *v.* FLAX.

RHAMNAZIN *v.* PERSIAN BERRIES (COLOURING MATTERS).

RHAMNETIN *v.* PERSIAN BERRIES (COLOURING MATTERS).

RHEA *v.* CHINA GRASS.

RHEONINE N (B.). An acridine colour. *Tetramethyl triamidophenyl acridine hydrochloride*. 1894. Brown powder, soluble in water, with a brownish-yellow colour. Alcoholic solution, bright yellow with green fluorescence. In concentrated H_2SO_4, brown solution, with green fluorescence; on dilution, brownish-red solution, with orange-.ed fluorescence.

Application.—A basic colour. Dyes tannin-mordanted *cotton* or *leather* brownish-yellow.

RHODAMINE B, B EXTRA (B.) (S.C.I.) (M.). *Rhodamine O* (M.), *Safraniline* (G.). A pyronine dye. *Hydrochloride of diethyl meta-amidophenol phthaleïn*. 1887. Green crystals or reddish-violet powder, soluble in water, with a bluish-red colour, which has a strong fluorescence when dilute. Alcoholic solution, bluish-red with orange fluorescence. In concentrated H_2SO_4, yellowish - brown solution with evolution of hydrochloric acid; on dilution, the solution becomes scarlet, and finally bluish-red.

18

Application.—A basic colour. Dyes *wool* and *silk* fast bluish-red with strong fluorescence. Dyes tannin-mordanted *cotton* red without fluorescence.

RHODAMINE 3 B (B.) (S.C.I.). *Anisoline* (Mo.). *Ethyl ether* of the preceding. 1891. Brownish-red powder, giving a violet-red solution in water, which, when dilute, has a strong brownish-red fluorescence. Alcoholic solution, bluish-red solution with orange fluorescence. In concentrated H_2SO_4, greenish-yellow solution, which becomes red on dilution.

Application.—As RHODAMINE B, but dyes bluer shades.

RHODAMINE G and G EXTRA (B.) (S.C.I.). Contains one ethyl group less than Rhodamine B. 1891. Yellowish-red powder, soluble in water with a red-violet colour with red fluorescence. Alcoholic solution, bluish-red with orange fluorescence. In concentrated H_2SO_4, yellow solution, which becomes fluorescent when diluted.

Application.—As RHODAMINE B, but dyes yellower shades.

RHODAMINE 6 G (B.) (S.C.I.). Contains two ethyl groups less than Rhodamine 3 B. 1892. Yellowish - brown or red powder, soluble in water with a scarlet colour with green fluorescence. Alcoholic solution, pink with yellow fluorescence. In concentrated H_2SO_4, red solution, which becomes yellow on dilution.

Application.—As RHODAMINE B, but dyes much yellower shades. On tannin-mordanted *cotton* the shade resembles that of *Safflower*.

RHODAMINE O (M.) *v.* RHODAMINE B.

RHODAMINE S (B.) (S.C.I.) (By.). *Diethyl meta-amido phenol succineine.* 1887. Green crystals or brown powder, soluble in water with a red colour with strong fluorescence. Alcoholic solution, pink with orange fluorescence. In concentrated H_2SO_4, yellowish-red solution without fluorescence; on dilution it becomes red.

Application.—Dyes unmordanted or tannin-mordanted *cotton* pinkish-red. Used also in dyeing paper pulp and wood.

RHODULINE RED B (By.). Dark brown powder. Aqueous solution, bluish-red; alcoholic solution, ditto, with orange fluorescence. Concentrated H_2SO_4, bright green solution; on dilution, becomes bluish-red.

Application.—A basic dye producing bright bluish-red shades on tannin-mordanted *cotton*.

RHODULINE RED G and RHODULINE VIOLET are similar colours.

RICINOLEIC ACID, *Oxyoleic acid*, $C_{18}H_{34}O_3 = C_{17}H_{32}(OH)(COOH)$, is a white crystalline mass which melts at 16° to 17°C. The glycerin ether, *ricinolein*, $(C_{18}H_{13}O_3)_3 C_3H_5$, is the chief constituent of castor oil, and yields the acid on saponification.

Ricinoleic acid takes up two atoms of bromine or iodine, but does not absorb hydrogen; neither does it absorb oxygen when exposed to the air.

Similarly to oleic acid, oxyoleic acid possesses the property of becoming polymerised, thereby forming a compound of a greater molecular weight. This reaction may be brought about by the action of nitrous acid, the isomeride *ricinelaidic* acid (a solid substance) being formed.

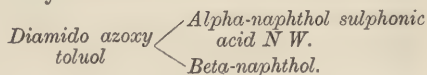The products of polymerisation play an important part in the production of Turkey-red.

Ricinoleic acid cannot be distilled, even under diminished pressure, without undergoing decomposition.

Ricinoleic acid is an oxyoleic acid, and differs from oleic acid in its behaviour towards sulphuric acid.

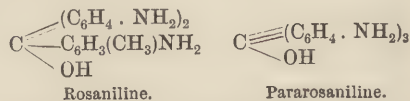**RICINOLEIN** *v.* TURKEY RED OIL.

ROCCELLIN *v.* FAST RED A.

ROCK SCARLET Y S (Br. S. & Sp.). An azo dye.

$$\text{Diamido azoxy toluol} \begin{cases} \text{Alpha-naphthol sulphonic acid } N\,W. \\ \text{Beta-naphthol.} \end{cases}$$

1892. Red powder, slightly soluble in water. In concentrated H_2SO_4, blue-red solution; on dilution, red ppt.

Application.—An acid colour. Dyes *wool* from an acid bath a red shade, fast to milling.

ROSANILINE (*triamido diphenyl tolyl carbinol*) and **PARAROSANILINE** (*triamido triphenyl carbinol*).

$$C \begin{cases} (C_6H_4 . NH_2)_2 \\ C_6H_3(CH_3)NH_2 \\ OH \end{cases} \qquad C \begin{cases} (C_6H_4 . NH_2)_3 \\ OH \end{cases}$$

Rosaniline.　　　　　Pararosaniline.

These bodies are not in themselves colouring matters, but a large number of dyes are derived from them. They are colourless bases which combine with acids to form strongly coloured salts (magenta).

Georgievics [*] considers that these bases can exist in two isomeric forms :—1st, as a colourless carbinol derivative; 2nd, as an ammonium base, which is as strongly coloured as the rosaniline salts. This view has not, however, met with general acceptance. H. Weil [†] directly controverts the statement, and considers the ammonium base above-mentioned to be a mixture of rosaniline and magenta.

ROSANAPHTHYLAMINE *v.* MAGDALA RED.

ROSAZINE (P.). An acid colour, giving bluish-red shades on *wool* or *silk*.

ROSE B (water soluble) (L.) *v.* ERYTHROSINE.

* *Mitt. Tech. Gew. Mus.*, vol. iv., p. 205; *Journ. Soc. Dyers and Col.*, 1895, p. 79.
† *Berl. Ber.*, 1896, p. 2677; *Journ. Soc. Dyers and Col.*, 1897, p. 38.

ROSE BENGALE (B.) (Fi.). *Rose Bengale N* (C.), *Rose Bengale A T* (Ber.), *Rose Bengale G* (M.). A fluoresceïn derivative. *Potassium salt of tetra-iododichlorfluoresceïn.* 1875. Brown powder. Aqueous solution, cherry-red without fluorescence; alcoholic solution red with yellow fluorescence. Concentrated H_2SO_4, brownish-yellow solution, which evolves iodine on heating; on dilution, brownish-red flocculent ppt.
Application.—An eosin colour. Dyes *wool* from slightly acid bath bluish-red.
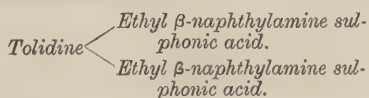
ROSE BENGALE A T (Ber.) *v.* ROSE BENGALE (B.).

ROSE BENGALE B (L.). *Rose Bengale* (B.) (C.), *Rose Bengale 3 B* (M.). A fluoresceïn derivation. *Potassium salt of tetra-iodo tetrachlorfluoresceïn.* 1882. Brownish-red powder. Aqueous solution, bluish-red without fluorescence. Concentrated H_2SO_4, yellow solution; on dilution, flesh-pink precipitate.
Application.—An eosin dye. Dyes *wool* bluish-pink or red.

ROSE BENGALE G (M.), **N** (C.) *v.* ROSE BENGALE (B.).

ROSE J B (alcohol soluble) (S.C.I.) *v.* EOSIN S.

ROSEAZURIN B (By.) (L.). An azo dye.

Tolidine
  Ethyl β-naphthylamine sulphonic acid.
  Ethyl β-naphthylamine sulphonic acid.

1886. Brown powder. Aqueous solution, cherry-red; alcoholic solution, bluish-red. Concentrated H_2SO_4, blue solution; on dilution, violet ppt.
Application.—A direct cotton dye. Dyes unmordanted *cotton* bluish-red.

ROSEAZURIN G (By.) (L.). Similar to above.

Tolidine
  Ethyl β-naphthylamine sulphonic cid.
  β-naphthylamine sulphonic acid.
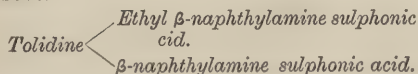
1886. Reddish-brown powder. Aqueous solution, cherry-red; alcoholic solution, crimson. Concentrated H_2SO_4, blue solution; on dilution, reddish-violet precipitate.
Application.—A direct cotton dye. Gives somewhat redder shades than mark B.

ROSEINE (Br. S.) *v.* MAGENTA.

ROSELIN B, G, 3 G, R (M.). 1893.

ROSINDULINE 2 B (K.). *Azocarmine B* (B.). An azine dye. *Phenyl rosinduline trisulphonate of soda.* 1890. Red-brown powder, slightly soluble in water with a bluish-red colour. Alcoholic solution, bluish-red. In concentrated H_2SO_4, green solution; on dilution, bright bluish-red.
Application.—An acid dye. Dyes *wool* bright bluish-red.

ROSINDULINE G (K.). An azine dye. *Rosindone monosulphonate of soda.* 1890. Red powder. Aqueous solution, red; alcoholic solution, orange-red. Concentrated H_2SO_4, dirty green solution; on dilution, brown, then orange-yellow.
Application.—An acid dye. Dyes *wool* orchil-red.

ROSINDULINE 2 G (K.), Isomeric with previous colour. 1890. Scarlet powder. Aqueous solution, scarlet; alcoholic solution, orange-red. Concentrated H_2SO_4, dirty green solution; on dilution, first yellow, then orange-red.
Application.—An acid colour. Dyes *wool* orange-red.

RÔSOLAN (P.). *Mauve, Mauveine, Chrome violet, Aniline purple, Perkin's violet, Tryaline, Violeine.* An oxidation product of aniline. *Hydrochloride of mauveine or its homologues.* 1856. Interesting as being the first coal-tar dye commercially manufactured. Reddish-violet paste, soluble in hot water with violet-red colour; soluble in alcohol. Concentrated H_2SO_4, olive-green solution; on dilution, becomes green, blue, and finally violet.
Application. — Dyes *silk* reddish-violet. Used in tinting white silk; used also for colouring postage stamps.

ROSOLIC ACID *v.* AURINE.

ROSOPHENINE GERANINE (Cl. Co.). 1899. Direct cotton colour.

ROSOPHENINE PINK 10 B (Cl. Co.). A direct cotton colour.

ROSOPHENOLINE *v.* CORALLINE.

ROUGE *v.* IRON (FERRIC OXIDE).

ROUILLE = Fr, NITRATE OF IRON.

ROXAMINE (D. & H.). An azo dye.

Naphthionic acid — Dioxynaphthaline.

1889. Red powder. Aqueous solution, scarlet-red; alcoholic solution, bright red. Concentrated H_2SO_4, violet solution; on dilution, bluish-red, then red.
Application.—An acid colour. Dyes *wool* orchil red.

RUBEOSINE. An obsolete fluoresceïn derivative.

RUBERYTHRIC ACID *v.* MADDER (CHEMISTRY OF).

RUBIAN *v.* MADDER (CHEMISTRY OF).

RUBINE *v.* MAGENTA.

RUBINE S *v.* ACID MAGENTA.

RUFIGALLIC ACID *v.* GALLIC ACID.

RUFIGALLOL (B.). An anthracene derivative. *Hexaoxyanthraquinone.* Brown powder, insoluble in water. Concentrated H_2SO_4, red solution.
Application. — A mordant dye. Dyes chrome-mordanted *wool* brown.

RUSSIAN GREEN (L.) *v* DARK GREEN (B.).

S

SAFFLOWER is the bloom of a peculiar thistle, *Carthamus tinctorius.* It contains a large amount of useless yellow colouring matter and a small amount of a red colouring matter, *carthamin,* which, until recently, was the only dye used in dyeing the red tape so commonly employed in tying up documents, &c. It is applied to *cotton* in the following manner :—The safflower is macerated in a salt solution until yellow colouring matter is no longer extracted, the liquid being rejected. The pasty mass is then extracted with dilute carbonate of soda solution, in which the cotton is subsequently worked. When most of the colouring matter is taken up by the cotton, the bath is acidified with tartaric acid, and, after working a few moments, the cotton is washed and dried. Safflower can be applied to silk in a similar manner, but is unsuitable for dyeing wool.

SAFFRON is obtained from the pistils and stigmata of the flower, *Crocus sativus,* which is grown in Europe generally. It contains an orange colouring matter, *saffronin* or *crocin,* which also exist in *Gardenia grandiflora.* Saffron is used as a condiment and in pharmacy.

SAFFRON SUBSTITUTE. Old name for *Victoria yellow.*

SAFRANILINE (G.) *v.* RHODAMINE B.

SAFRANINE (G.) (F.) (D. & H.) (C.R.). *Safranine T* (B.), *Safranine extra G* (Ber.). *Safranine G G S* (C.), *Safranine F F extra N O* (By.), *Safranine concentrated* (M.), *Safranine A G extra* (K.), *Safranine S* (C.), *Aniline rose.* Mixtures of phenyl and tolyl safranines. Azine derivatives. 1863. Reddish - brown powder. Aqueous solution, red ; alcoholic solution, red with yellowish fluorescence. Concentrated H_2SO_4, green solution ; on dilution, blue and finally red.

Application.—A basic colour. Dyes tannin and tartar emetic prepared *cotton* red.

SAFRANINE B EXTRA (B.). *Phenosafranine.* The pure *phenyl* compound (see above). 1878. Green crystals.

Reactions and Application.—As above.

SAFRANINE SCARLET. Mixture of *Auramine* and *Safranine.*

SAFRANISOL (K.). *Methoxy safranine.* Obsolete.

SAFROSIN (S.C.I.) (Br.S.) *v.* EOSIN B N.

SAINT MARTHA WOOD *v.* REDWOODS (SOLUBLE).

SAL AMMONIAC *v.* AMMONIUM CHLORIDE.

SAL VOLATILE *v.* AMMONIUM SESQUI-CARBONATE.

SALICENE YELLOW G, 2 G (K.). Mark G. Yellowish-brown powder. Aqueous and alcoholic solution, bright yellow.

Concentrated H_2SO_4, crimson solution ; on dilution, yellow ppt., which re-dissolves on further dilution to bright yellow solution.

Application.—Acid mordant dyes, giving bright greenish-yellow on *wool.*

SALICIN RED B, G, 2 G (K.). Acid mordant colours, giving bright red shades on *wool.* When saddened with fluorchrome, colours are very fast to milling.

SALICYLIC ACID. $C_6H_4{<}^{OH}_{COOH}$. A derivative of phenol. Used as a preservative in thickeners, &c., on account of its antiseptic properties.

SALICYL ORANGE and YELLOW. Obsolete nitro compounds.

SALMON PINK. A mixture of *Eosin dyes.*

SALMON RED (B.). An azo dye. *Action of* $COCl_2$ on product of

$$Diamidodiphenyl\ urea{<}^{Naphthionic\ acid.}_{Naphthionic\ acid.}$$

1888. Brown powder. Aqueous solution, orange - yellow. In concentrated H_2SO_4, magenta - red solution ; on dilution, violet ppt.

Application.—A direct cotton dye. Dyes unmordanted *cotton* flesh colour to brownish-orange.

SALT *v.* SODIUM CHLORIDE.

SALTCAKE *v.* SODIUM SULPHATE.

SALT OF HARTSHORN *v.* AMMONIUM CARBONATE.

SALTPETRE *v.* POTASSIUM NITRATE.

SALTS OF SORREL *v.* POTASSIUM BINOXALATE.

SANDALWOOD, SANDERSWOOD *v.* REDWOODS (INSOLUBLE).

SANTALIN *v.* REDWOODS (INSOLUBLE).

SAPAN LIQUOR *v.* REDWOODS (SOLUBLE).

SAPAN WOOD *v.* REDWOODS (SOLUBLE).

SAP GREEN is a product of the fruit of *Rhamnus catharticus.* The ripe berries are submitted to pressure, and the purple juice thus obtained is treated with alkali, when it becomes green. It is employed in confectionery and in paper staining.

SAPONIFIABLE MATTER *v.* LUBRICATING OILS (ANALYSIS).

SAPONIFICATION *v.* OLEIN, PALMITIN, AND SOAP.

SAPONIFICATION EQUIVALENT OF FATTY ACIDS *v.* SOAP ANALYSIS.

SAW-WORT (*Serratula tinctoria*), which grows abundantly in meadows, affords a very fine pure yellow colour with alum mordant, which greatly resembles weld yellow. It is extremely permanent.

SCARLET (F.) *v.* COCHINEAL RED A (B.).

SCARLET B (O.) *v.* PONCEAU 3 R B (Ber.).

SCARLET E C (C.) *v.* PONCEAU 3 R B (Ber.).

SCARLET FOR COTTON. A mixture of *Safranine* and *Chrysoidine*.

SCARLET FOR SILK (M.) *v.* DOUBLE BRILLIANT SCARLET G.

SCARLET G (C.). *Ponceau G* (C.). An azo compound.

Xylidine — β-naphthol disulphonic acid G.

1878. Brownish-red powder. Aqueous solution, bright red. Concentrated H_2SO_4, cherry-red solution ; on dilution, orange.

Application. — An acid dye, producing yellowish-scarlet shades on *wool*.

SCARLET G R (By.) *v.* BRILLIANT ORANGE R.

SCARLET J, JJ, and V (Mo.) *v.* EOSIN B N.

SCARLET R (By.) *v.* BRILLIANT ORANGE R.

SCARLET 6 R (M.) (B.) *v.* PONCEAU 6 R.

SCHAEFFER'S ACID *v.* NAPHTHOL (BETA-NAPHTHOL MONOSULPHONIC ACID).

SCHEELE'S GREEN *v.* COPPER ARSENITE.

SCHLIEPER'S PROCESS *v.* ALUMINIUM (SODIUM ALUMINATE).

SCHÜTZENBERGER'S SALT *v.* SODIUM HYDROSULPHITE.

SCHWEITZER'S SOLUTION *v.* COPPER (CUPRIC HYDROXIDE).

SCUTCHING *v.* FLAX.

SERGE BLUE. A low quality *Alkali blue*.

SERICINE, SILK GUM *v.* SILK.

SESAME OIL *v.* SOAP.

SETOCYANIN (G.). A basic bright blue dye.

SETOGLAUCIN (G.). A basic greenish-blue dye.

SETOPALINE (G.). A bright basic blue, suitable for silk dyeing.

SHELLAC *v.* LAC DYE.

SILK. The term *silk* is applied to the fibrous substance produced by various insects for the purpose of forming a "cocoon," or nest, in which they pass the chrysalis stage of their existence. Silk differs entirely from all other natural fibres in that it is entirely devoid of cellular or organised structure, being, in fact, a solidified liquid.

Origin. — Many varieties of silk are commercially distinguished, and these may conveniently be classified into (1) *cultivated*, and (2) *wild* silks ; the former being much the most important.

The principal species of silkworm is *Bombyx mori*, or mulberry silkworm, which is cultivated in Southern Europe, China, Japan, India, &c.

Culture. — The female insect lays 200 to 500 eggs, which in size and appearance resemble poppy seeds. One ounce of eggs contains about 40,000, but only 50 to 70 per cent. yield caterpillars.

In the hotter countries the worms are reared in the open air, but in Europe this takes place in specially constructed buildings, termed *magnanaries*, in which the eggs are spread on sheets of white paper on shelves. The temperature of the rooms must be carefully regulated, and is raised in twelve days from 18° to 25° C.

At the end of this period hatching commences, and the young insects are at once taken to another room, where they are systematically fed for about a month on the leaves of the white mulberry (*Morus alba*). During this period the caterpillars eat enormously and grow with such rapidity that they cast their skins every four or five days, and eventually increase to from 4000 to 5000 times their original size, attaining a length of from 3 to 4 inches and a weight of $1\frac{1}{4}$ to $1\frac{3}{4}$ ounces.

About the thirty-third day they cease to feed, and are placed on birch twigs where they spin their cocoons. The spinning lasts about three days, and, when complete, some of the finest cocoons are kept for breeding and the rest are killed by steaming or stoving, after which they are brought into the market.

The substance from which the fibre is produced is present in the form of a clear, colourless, sticky liquid in the *silk glands* of the worm, which are symmetrically placed on either side of the body and communicate with a capillary orifice in the head near the spinneret. According to Duseigneur, each gland is double, and contains two liquids which ultimately form the *fibroin* and *sericine* respectively.

On issuing from the spinneret and consequent exposure to air the silk liquids solidify and form a double fibre, which consists of a thread from each gland cemented together along their length.

Reeling. — This process consists in combining together the fibres from a number of cocoons to form a single thread. The cocoons are placed in water heated to about 60° C., which softens the cementing material. From 4 to 18 fibres are then collected by the operator and reeled off into a single continuous thread, the softened silk-gum causing the fibres to cohere. Fibres from fresh cocoons are introduced as often as necessary to maintain the thickness of the thread.

Organzine, or warp silk, is obtained by using 12 to 18 fibres and imparting considerable twist to the thread, while *tram*, or weft, silk is thinner and contains less twist. Reeled silk is thus the raw material for the manufacture of the best silk material.

The outer sheath and innermost layer of the cocoon consist of a tangle of fibres, and cannot be reeled. This remark also applies to pierced cocoons used in breeding, double, or otherwise defective cocoons, and such as are spoilt in steaming. These are all boiled with water, then with soda, then washed and dried, and finally torn to shreds and carded

and spun; the material thus produced being known as *spun silk*. *Chappe* silk and *Flos* silk are similar products.

Counts.—In *thrown* or *reeled* silk the counts indicate the weight per hank of 1000 yards. For spun silk the counts are as for cotton (see *cotton*).

Structure of Silk Fibre.—Raw silk (reeled fibre) has the appearance of a uniform thread, cream or yellow in colour and of little lustre. A single fibre as drawn from the cocoon varies in length from 500 to 1500 yards, and in diameter from 0·01 to 0·02 mm. The fibre from the outer portion of the cocoon has the greatest diameter and the thickness gradually decreases as the silk-glands of the worm become exhausted, which causes the inner portion of the cocoon to afford thinner fibre.

A cross section of an individual raw fibre shows that it consists of two approximately cylindrical threads cemented together along their length, being, in fact, a double fibre. By boiling with soap the two fibres are separated, and each single fibre then appears as a structureless, transparent, glossy, cylindrical fibre.*

Physical Properties.—The chief physical properties of silk are *lustre, strength, elasticity*, and *avidity for moisture*.

In *lustre* silk is pre-eminent, this beautiful quality being due to the smooth glassy character of its exterior. The effect is increased by the transparency of the fibre.

In *strength* and *elasticity* raw silk greatly exceeds "boiled-off" silk, the strength decreasing 30 per cent. and the elasticity 45 per cent. by removing the silk-gum. The low tensile strength of all forms of *artificial silk* and the lack of elasticity shown in the creasing of mercerised cotton shows that there is not as yet any textile fibre in the market with the same valuable properties as natural silk.

Silk has a specific gravity of 1·367. It is a bad conductor of electricity, and hence is difficult to manipulate in a very dry atmosphere.

Avidity for Moisture.—Silk will absorb as much as 30 per cent. of moisture without feeling wet, and since it is a costly fibre and is sold by weight it is important to know its hygrometric condition when buying, and this has resulted in the establishment of conditioning houses. (*v.* CONDITIONING.)

Chemical Composition.—Raw silk is not a uniform substance, but is composed of two concentric layers, the innermost, or core, constituting the fibre proper, and the exterior being composed of a gum-like substance.

The fibre substance is termed *fibroine*. Its composition corresponds to the formula $C_{15}H_{23}O_6N_5$, and though its constitution is unknown it shows, like wool, the properties of an amido acid.

* Wild silk differs, v. WILD SILK.

Chemical Properties.—When heated in a dry tube, silk commences to turn brown at about 150° C., becoming black at about 235° C. When burnt it gives off a smell of burnt feathers and leaves a bulky residue of carbon.

Action of Water.—Fibroine is insoluble in water at ordinary temperatures but dissolves if heated in a sealed tube with water to 170° C., forming a colourless limpid solution.

Action of Acids.—Silk is easily soluble in concentrated *sulphuric* or *hydrochloric* acid, forming a colourless solution, and with *nitric* acid it forms a yellow solution.

Silk absorbs acids from their dilute aqueous solution and retains them tenaciously. The fibre at the same time acquires increased lustre and a peculiar feel, emitting, when squeezed, a peculiar crunching sound. Silk in this condition is termed *scroop silk*, and may be produced by working the silk in dilute tartaric, acetic, or sulphuric acid, and drying without washing.

Silk is soluble in *glacial acetic* acid or in *molten citric* or *oxalic* acid. It is turned yellow by *dilute nitric* acid. Dilute acids in boiling solution remove the silk-gum from raw silk, but are little used for that purpose.

Like wool, silk is readily dissolved by *caustic alkalies* under suitable conditions of temperature and concentration. Very dilute or very concentrated solutions have, however, little action, and the effect of caustic alkali of any strength is very slight at temperatures approaching 0° C.; this fact being made use of in the mercerisation of mixed silk and cotton fabrics.

Ammonia or its salts have little action on silk. *Alkaline carbonates* have also little action unless of considerable strength and in boiling solution.

Soap has no injurious action on silk, even in concentrated boiling solution.

Action of Oxidising Agents.—Strong solutions of *chromic acid* dissolve silk. *Bichromate of potash* oxidises and weakens the fibre. *Permanganate of potash* has a similar action, but in dilute solution is used as a bleaching agent. On steeping the fibre in dilute permanganate it gradually acquires a brown colour, owing to the deposition of hydrated manganic oxide, but on removing this by sulphurous acid the colour of the silk is found to be improved.

Chlorine and *hypochlorites* in strong solution attack and destroy the fibre, but in very dilute solution they impart to the silk an increased affinity for colouring matters. The action is, however, less than in the case of wool.

Like wool, silk absorbs metallic salts from their solutions; but whereas in the case of wool fibre it is usually necessary to heat to the boil before much fixation occurs, silk is capable of attracting metallic compounds from

cold solutions if moderately concentrated. This phenomenon plays a most important part in the mordanting and weighting of silk.

A concentrated solution of zinc chloride 140° Tw. dissolves silk, and the solution may be diluted with weak hydrochloric acid without precipitation. On dialysing this liquid the zinc chloride and acid are removed and an aqueous solution of silk remains, which, when evaporated, leaves a brittle resinous residue which will not re-dissolve in water.

Silk is soluble in ammoniacal cupric hydrate or ammoniacal nickel hydrate solution. A solution prepared by dissolving 16 grms. copper sulphate in 150 c.c. water, adding 8 to 10 grms. glycerin, and then caustic soda until a clear solution is obtained, dissolves silk without affecting wool or cotton.

Tannic acid and *sugar* are absorbed by silk, and are used in weighting.

Action of Colouring Matters.—Generally speaking, the affinity of silk for dyes is similar to, but weaker in character than, that of wool. In a boiling solution wool has a much greater affinity than silk, but in cold baths wool dyes very little or not at all, while with suitable dyes full shades may be obtained on silk.

Silk Gum, Silk Glue, Sericine.—These names are applied to the gummy matter which envelopes the raw silk fibre, cementing the two single fibres together. In composition it is closely allied to *Fibroine*, the relationship being indicated by the following formulæ :—

$$C_{15}H_{23}N_5O_6 + H_2O + O = C_{15}H_{25}N_5O_8$$
Fibroine. Sericine.
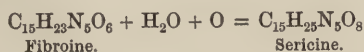
Sericine is highly gelatinous, a 1 per cent. solution gelatinising on cooling. It is precipitated from its aqueous solution by alcohol, tannic acid, and many metallic salts. It is soluble in hot water, more easily in caustic soda or soap solution and in dilute acids.

The colouring matter of naturally yellow silk resides in the sericine. Dubois states that the colouring matter is of a composite character, but contains *carotin* (*q.v.*) as one of its constituents.

Wild Silks.

There are a very large number of wild silks, India affording upwards of fifty known species. The most important is Tussur (*Tussah, Tusoa, Tasar*), of which the caterpillar and moth, *Antherea mylitta*, are much larger than *Bombyx mori*, and the cocoons also are about four times the size of mulberry cocoons. They are not found single, but in large pocket-shaped masses attached to the trees in the jungle. The cocoons are impregnated with uric acid, which is removed by alkali before spinning. Tussur has been an article of commerce in India for thousands of years. It comes into the market, to a small extent, as reeled silk, but much more largely as spun silk.

The fibre is double, as in cultivated silk. It is about four times coarser, and therefore stiffer and stronger than mulberry silk, and is largely used for plushes and other pile fabrics. Each of the threads composing the double fibre can by suitable treatment be split up into 6 or 8 fibrillæ.

Under the microscope, tussur appears not unlike cotton, being flat and band-like in character. It is, however, much more transparent than cotton.

Chemical Composition and Properties.—Raw tussur contains about 5 per cent. of ash, a much larger amount than cultivated silk. Its percentage composition also appears to differ somewhat from that of the latter.

				Tussur Silk.	Mulberry Silk.
Carbon,	.	.	.	47·18	47·78
Hydrogen,	.	.	.	6·30	6·23
Nitrogen,	.	.	.	16·85	18·90
Oxygen,	.	.	.	29·67	26·04

Action of Alkalies.—Tussur is much less easily affected by caustic soda than mulberry silk. A boiling 10 per cent. solution of NaOH easily dissolves ordinary silk, but attacks tussur very slowly.

Acids and Salts.—Tussur is also much more resistant than cultivated silk towards acids. Concentrated hydrochloric acid dissolves the latter almost instantly, but tussur is little affected after many hours. Concentrated zinc chloride solution also attacks tussur very slowly.

Even after removing the gummy matter by soap, tussur possesses a pale buff colour which is difficult to remove. It is more difficult to dye than ordinary silk, being, in fact, in all respects a more inert body.

Other varieties of tussur are produced in China (*Antheræa pernyi*), Japan, and other countries.

Of other wild silks, the following may be mentioned :—

Antherea Assama, found in Assam; the fibre is known as "*Muga silk.*" The caterpillar feeds on the mangrove and gives a golden yellow cocoon.

Antherea yamamai is indigenous to Japan, and is very similar in appearance and properties to ordinary silk, but coarser.

Attacus cynthia feeds on the castor-oil plant, and produces a white fibre.

Attacus atlas, a variety cultivated in China, is the largest and most beautiful of the silk

moths, attaining a size of 6 inches across the wings. The caterpillar spins a cocoon as large as a hen's egg, and covered at both ends with very thick fibre known as *Tagara silk.*

Two Japanese varieties, Ailanthus and Yamamai, were until recently reserved for the exclusive use of the Mikado, and exportation of their eggs was a capital offence. They are now being cultivated in France with a considerable degree of success.

Sea Silk or Byssus is the product of certain molluscs, principally *Pinna nobilis* and *P. rudis.* It is collected chiefly in Sardinia and Corsica. The fibres have the object of attaching the molluscs to the rocks. They are of a golden brown colour, very soft, elastic, durable, and glossy. The substance has not been investigated, but differs from ordinary silk by being insoluble in acids and alkalies.

SILK, ARTIFICIAL. The silk fibre being devoid of cellular structure, and consisting, indeed, of the solidified liquid contents of the silk glands of the worm, obviously offers a much more promising field to experimenters who attempt to imitate it artificially than do the highly-organised fibres of wool and cotton.

In its broadest outlines the problem of the production of an artificial fibre resembling silk is not a difficult one. Given a suitable viscous liquid, all that is necessary is to convert this into the form of thin threads, which must, of course, be insoluble in water and of sufficient strength to withstand the weaving and other manufacturing processes and so produce a useful fabric.

The second part of the problem—the production of the thread—offers no very serious difficulty, the selected liquid being forced by pressure through fine orifices into some medium which causes it to solidify. The nature of the coagulating or solidifying medium depends upon the character of the original liquid, and may be water, acetic acid, ammonia, or even hot air.

The composition of the viscous solution may be such as to correspond, more or less closely, with that of natural silk, or may be of an entirely different character. The first artificial filament produced which resembled silk in appearance was spun glass, fabrics of brilliant lustre and considerable softness and elasticity being produced from this substance. Such fabrics are, however, of little value, since they rapidly become disintegrated on account of the brittleness of the fibre—the minute particles of glass which are continually separated from such fabrics being, moreover, highly injurious when inhaled.

Many attempts have been made to produce "artificial silk" from cellulose as a basis.

This substance as recovered from its solution dries up under suitable conditions into a lustrous, horny mass, which, when in the form of fibre, greatly resembles silk in appearance. "Artificial silk" may therefore be obtained by suitable means from any of the known cellulose solvents.

The earliest processes by which "artificial silks" were produced consisted, however, in coating cotton fibres with natural silk, the process being carried out by dissolving the latter in an acid or alkaline solution, and after impregnating the cotton with this solution, precipitating the silk by alkali or acid.

Much more important are the "*collodion silks*" produced from the nitro-celluloses, these being at the present time manufactured on a large scale. The production of a silk-like fibre in this manner was first patented by *De Chardonnet* in 1886, but the original product was very inflammable and deficient in elasticity and strength. It was prepared by treating cellulose with a mixture of nitric and sulphuric acids and dissolving the tetra-nitrate thus formed in a mixture of alcohol and ether. The clear solution of *collodion* obtained in this manner was placed in a copper vessel and forced by air pressure through a fine orifice into water, where it solidified in the form of a thread.

Subsequently, De Chardonnet took out several patents for improvements, the most important being the process of denitrating the fibre, and thereby rendering it less inflammable. This is brought about by treatment with one of the following solutions :—*Dilute nitric acid, ammonium sulphide,* or *alkaline thiocarbonates.* Another improvement consists in coagulating the solution by means of hot air instead of by water ("dry spinning"), which has the additional advantage of reducing the loss of the somewhat expensive solvent.

In dyeing properties, collodion silk holds an intermediate position between natural silk and cotton. Unlike cotton, it readily attracts basic dyes, and, unlike silk, it cannot be satisfactorily dyed with most acid colouring matters. Chardonnet's silk is largely employed in the manufacture of the black plush with which silk hats are covered.

Another process which is commercially employed for the production of collodion silk is connected with the name of *F. Lehner,* whose method of manufacture differs from Chardonnet's in several important details. The cellulose, in the form of cotton wool, is digested with ammoniacal copper solution before nitration, and the nitro-cellulose is dissolved in a mixture of ether, wood-spirit (methyl alcohol), and ethyl hydrogen sulphate. A very interesting observation of Lehner's had reference to the great effect upon the fluidity of the collodion, brought about by a small addition of sulphuric acid.

Still another process was patented by *De Vivier.* In this, solutions of (a) nitro-

cellulose in glacial acetic acid, (*b*) guttapercha in carbon bisulphide, and (*c*) isinglass in glacial acetic acid were mixed together along with glycerin and castor oil. This mixture was then converted into a thread, which was subsequently treated successively with solutions of carbonate of soda, albumen, mercuric chloride, and ammonia. This process does not appear to have been a commercial success.

Artificial fibres have also been prepared from solutions of cellulose in zinc chloride and ammoniacal copper oxide.

Dreaper and *Tompkins* dissolve purified cotton in a concentrated solution of zinc chloride, adding to the solution 2 to 5 per cent. of some calcium, barium, or strontium salt. The liquid is then forced through orifices into alcohol or acetone, which precipitates the cellulose in the form of a thread and dissolves the metallic salts.

By hydrolysing cellulose with sulphuric or phosphoric acid *Pauly* obtained a syrupy solution, but states that it is not possible to obtain useful fibre from such a solution. As a suitable solvent he therefore proposes the cuprammonium solution, which has for so long a time been known to have a great solvent action on cellulose. In Pauly's process the cellulose solution thus prepared is forced through spinerettes into acetic acid.

This product is now manufactured on a large scale, and sold under the name of "Glanzstoff" or "Bronnert's silk," Pauly's original process being modified in several particulars.

Viscose Silk is the name which has been applied to the fibre produced from *Cross and Bevan's* cellulose xanthate. The xanthate is prepared by treating mercerised cotton with carbon bisulphide, and a solution of this product in water possesses great viscosity. On drying, the xanthate decomposes, and the regenerated cellulose forms a highly-lustrous film or thread.

Mention must also be made of one or two products which are not derived from cellulose, but from gelatine or glue. In one process gelatine is dissolved in a hot solution of bichromate of potash, the action of the bichromate being to render the gelatine insoluble after exposure to light. The solution is forced by air pressure through fine orifices, and the threads thus formed are carried by a revolving drum on to an endless band, and exposed to the action of light for the necessary length of time. The elasticity, pliability, and strength of the thread can be varied by the addition of glycerin, castor oil, or other suitable medium.

Vandura Silk is also obtained by the use of gelatine as a basis, but the product is rendered insoluble in this case by treatment with formaldehyde vapour instead of the combined action of chromic acid and light. The process of manufacture involves two main operations — the production of the thread, and the rendering of this thread insoluble.

The first part of the process is carried out by preparing a very concentrated solution of gelatine, which is melted by heat and forced through spinnerettes on to an endless travelling band, long enough to allow the threads to become dry. The threads then pass into a closed chamber, where they are subjected for some hours to the action of formaldehyde vapour. Vandura silk is a beautifully lustrous fibre, and in the dry state is fairly strong and elastic. When wetted with hot water, however, it becomes extremely tender, and is therefore at present more adapted for purposes of ornamentation than for use as a textile fibre.

SILK BLUE (M.) *v.* SOLUBLE BLUE.

SINGLE MURIATE OF TIN *v.* STANNOUS CHLORIDE.

SIZES. The object of sizing yarn is to strengthen it so that it may the better withstand the weaving process, and to weight it.

Hugh Monie, Jr.,[*] divides the substances used for this purpose into :—I. The adhesive substances which attach the size to the yarn ; II. Weighting bodies ; III. Compounds added to preserve the softness of the yarn ; IV. Antiseptics to prevent mildew.

I. Wheat, farina (see below), rice, and sago flours come under the category of adhesive substances.

Wheat flour varies considerably in quality, and is often mixed with other flours, starchy matter, &c. A sample on boiling with water should not be dark in colour. The amount of gluten present is of primary importance.

Estimation of Gluten. — Wanklyn and Cooper (*Bread Analysis*) take for this determination 10 grms. of flour, and wash it carefully free from starch. The gluten is then immersed in ether and worked with the aid of a glass rod. The mass is subsequently spread out in a platinum basin and dried in the water oven until of constant weight. A correction of 1 per cent. on the flour for fat and 0·3 per cent. for ash must be made. Hence the percentage of insoluble matter found as above, less 1·3, is the amount of gluten.

Farina is the starch obtained from potatoes. The potatoes are shredded and the starch washed out and allowed to subside in tanks of water. The product is then dried, and ground. Farina has a glistening appearance and crisp feel. The amount of water in farina is generally about 20 per cent. Farina imparts a certain amount of coarseness to the goods. When boiled with water it forms a thicker paste than any other starch.

[*] *Sizing Ingredients, Size Mixing, and Sizing.*

Rice flour is simply rice ground to a fine powder.

Sago flour is obtained from certain palms by a process similar to that employed in the preparation of potato starch.

All the flours mentioned above have a tendency to cause mildew. This is obviated to some extent by steeping the flour in water for some days before use, with occasional stirring. If putrefaction commences the addition of carbolic acid will arrest it.

II. · Weighting Substances. — These include the sulphates of sodium, magnesium, calcium, and barium, together with China clay.

China clay or Kaolin is a soft, friable, white mineral found in the South of England, and in China and Japan. The crude product is washed in a stream of water to free it from gritty matter. The absence of grit is essential for sizing purposes.

Aniline blue, indigo, and *Prussian blue* are added to sizes in order to destroy the dirty colour which they impart to the yarn.

III. Softeners are employed to prevent the sizing from falling off the yarn, and to cause the fibre to remain soft instead of becoming harsh and hard. Castor oil is one of the most frequent additions; magnesium chloride and tallow, paraffin wax, and light coloured soaps (either soft or hard and of good quality) are used. Crude glycerin is a good softener, but its dark colour precludes its general use. The chlorides of magnesium and zinc are employed as softeners; they possess deliquescent and antiseptic properties.

The composition of softening soaps is detailed under SOAP.

Paraffin wax is prepared by fractionating and otherwise purifying in a systematic manner the products obtained by distilling shale. The purified substance is white and translucent, and the melting point is usually about 120° F. (49° C.).
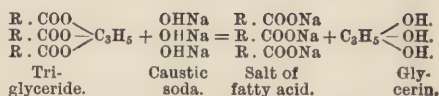
Paraffin wax cannot be used in sizing goods which require subsequent dyeing, bleaching, or printing.

SLAKED LIME *v.* CALCIUM HYDROXIDE.

SLOELINE *v.* INDULINE.

SOAP. Soaps are salts of fatty acids formed by the decomposition of vegetable and animal oils and fats, consisting of glycerides of the fatty acids.
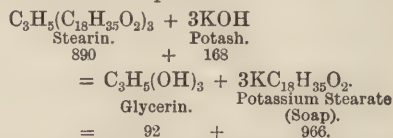
When the glycerides are decomposed, or "saponified," by treatment with strong bases, the salts of the fatty acids which are present are produced, and glycerin is liberated. The reaction may be explained by the following general formula, in which R stands for any fatty acid radical. One molecule of the triglyceride requires three molecules of caustic soda for saturation, yielding three molecules of the sodium salt of the fatty acid and one molecule of free glycerin.

$$\begin{array}{ccccc}
R.COO \\
R.COO{>}C_3H_5 & + & OHNa \\
R.COO & & OHNa
\end{array} = \begin{array}{c}
R.COONa \\
R.COONa \\
R.COONa
\end{array} + C_3H_5{<}\begin{array}{c}OH.\\OH.\\OH.\end{array}$$

| Tri-glyceride. | Caustic soda. | Salt of fatty acid. | Gly-cerin. |

Lead and several other metals also form soaps, but the term "soap" is usually applied only to the sodium and potassium compounds. The soaps of the alkalies are soluble in water. Besides fats and oils, resin is used in conjunction with those substances in the preparation of soaps for bleaching calico and for household use. Resin soaps are avoided as a rule in the textile industries.
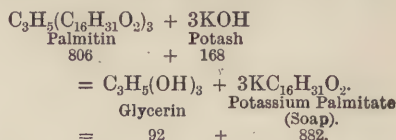
The fatty acids which are found most frequently in soaps are *stearic, palmitic,* and *oleic* from lard and tallow; *brassic* acid from rape oil, *lauric* acid from cocoa-nut oil, *linoleic* acid from linseed and other drying oils, and *ricinoleic* acid from castor oil.

The fatty acids are monobasic acids, but glycerin, the radical of which (C_3H_5) is combined with the fatty acids in neutral oils and fats, plays the part of a tri-acid base. It is a trihydric alcohol. When oils and fats are boiled with potash or soda saponification takes place, three molecules of alkali being required to displace one of glycerin. For example, stearin, which is essentially glyceryl tristearate (the chief constituent of mutton fat), undergoes the following change when boiled with caustic potash :—

$$C_3H_5(C_{18}H_{35}O_2)_3 + 3KOH$$

| Stearin. | | Potash. |
| 890 | + | 168 |

$$= C_3H_5(OH)_3 + 3KC_{18}H_{35}O_2.$$

| | Glycerin. | | Potassium Stearate (Soap). |
| = | 92 | + | 966. |

In this reaction 890 parts of stearin are decomposed by 168 parts of caustic potash, with the formation of 966 parts of anhydrous soap.

If palmitin or glyceryl tripalmitate (the chief constituent of palm oil) be treated in like manner a similar reaction takes place ; but, on account of the difference in molecular weights, the combining amounts are different, as shown by the following equation :—

$$C_3H_5(C_{16}H_{31}O_2)_3 + 3KOH$$

| Palmitin | | Potash |
| 806 | + | 168 |

$$= C_3H_5(OH)_3 + 3KC_{16}H_{31}O_2.$$

| | Glycerin | | Potassium Palmitate (Soap). |
| = | 92 | + | 882. |

In this case 168 parts of the potash decompose only 806 parts of fat (palmitin), with the production of 882 parts of anhydrous soap. And according to the glycerides present in oils or fats, more or less potash is required to effect saponification of a given weight of fatty matter. This may be expressed in two ways: either by the amount of potash required to

saponify 100 parts of the fatty matter, or the amount of oil or fat saponified by one equivalent of potash or soda. In the latter case the figure represents the "saponification equivalent" of the oil or fat. It is the quantity of oil or fat which is saponified by 56 parts of caustic potash, or 40 parts of caustic soda, and may be obtained by dividing the percentage of caustic potash required for saponification into 5600, or the percentage of caustic soda into 4000. In the case of fatty acids the saponification equivalents are identical with their molecular weights (fatty acids being monobasic), whereas with the triglycerides or neutral fats and oils the saponification equivalents are one-third of their molecular weight. The following table shows the saponification equivalents of the more important fatty acids, glycerides, natural oils and fats :—

FATTY SUBSTANCE.		Percentage of Potash (KOH) for Saponification.	Saponification Equivalent.
Lauric acid,	$C_{12}H_{24}O_2$,	28	200
Palmitic acid,	$C_{16}H_{32}O_2$,	21·88	256
Stearic acid,	$C_{18}H_{36}O_2$,	19·72	284
Oleic acid,	$C_{18}H_{34}O_2$,	19·85	282
Brassic acid,	$C_{22}H_{42}O_2$,	16·57	338
Linoleic acid,	$C_{16}H_{28}O_2$,	22·22	252
Ricinoleic acid,	$C_{18}H_{34}O_3$,	18·79	298
Laurin,	$C_3H_5(C_{12}H_{23}O_2)_3$,	26·38	212·7
Palmitin,	$C_3H_5(C_{16}H_{31}O_2)_3$,	20·88	268·7
Stearin,	$C_3H_5(C_{18}H_{35}O_2)_3$,	18·91	296·7
Olein,	$C_3H_5(C_{18}H_{33}O_2)_3$,	19·04	294·7
Brassein,	$C_3H_5(C_{22}H_{41}O_3)_3$,	16·00	350·7
Linolein,	$C_3H_5(C_{16}H_{27}O_2)_3$,	21·20	264·7
Ricinolein,	$C_3H_5(C_{18}H_{33}O_3)_3$,	18·06	310·7
Olive oil,		19 to 19·5	287 to 295
Cottonseed oil,		19·1 „ 19·7	284 „ 293
Rape oil,		17 „ 17·6	318 „ 330
Linseed oil,		18·7 „ 19·5	287 „ 300
Palm oil,		19·6 „ 20·2	277 „ 285
Cocoa-nut oil,		24·6 „ 26·8	208 „ 228
Tallow,		19·3 „ 19·8	283 „ 290
Castor oil,		17·6 „ 18·1	310 „ 319

Natural oils from the same sources have not always exactly the same composition. They are not chemical compounds, but mixtures of several compounds—the glycerides. The majority of fixed oils on saponification yield from 95 to 96 per cent. of fatty acids, and about 10 per cent. of glycerin. Fats containing much lauric acid give rather different results. The following table contains a few examples of the theoretical proportions of fatty acid and glycerin, resulting from the saponification of pure tri-glycerides :—

	100 parts of Glyceride yield	
	Fatty Acid.	Glycerin.
Laurin,	94·04	14·42
Palmitin,	95·28	11·41
Stearin,	95·73	10·34
Olein,	95·70	10·40
Brassein,	96·39	8·75
Linolein,	95·21	11·58
Ricinolein,	95·92	9·88

The increase in weight is due to what is termed "hydrolysis." On saponification the elements of water are taken up to form glycerin, and on decomposing the soap with a mineral acid, water also takes part in the reaction to form the fatty acids.

The following table (pp. 284, 285), compiled principally from Allen's *Commercial Organic Analysis*, shows the origin and chief properties of the more important oils and fats (with oleic acid and resin) used in the manufacture of soap.

As a rule, the higher the solidification point of an oil or fat the greater is the consistency of the soap made from it.

Soda forms much harder and firmer soaps than potash. In fact, all ordinary so-called *hard* soaps contain soda as a base, while *soft* soaps (often called "sweet" soaps) contain potash as the base. The hardest commercial soaps are those made with soda and fatty matter containing much stearic acid, such as tallow ; and the softest are those made with

OILS AND FATS USED IN SOAP MAKING.

NAME OF OIL.	Source.	Chief Components of Oil.	Specific Gravity at 15·5°C.	Solidification Point. °C.	Saponification Equivalent.	Lbs. of pure caustic potash required to saponify 100 lbs. of oil.	Lbs. of pure caustic soda required to saponify 100 lbs. of oil.	OTHER CHARACTERS, &c.
A. Of Animal Origin.								
BONE FAT,	Bones of various animals.	Olein and palmitin.	·915	..	284 to 294	19·1 to 19·7	13·6 to 14·1	Brownish colour; unpleasant smell. May contain calcium phosphate.
LARD,	From abdomen and other parts of the pig.	Olein, palmitin, and stearin.	(at $\frac{99°}{15\cdot5}$ C. ·860)	27 to 44	286 to 292	1·2 to 19·6	13·7 to 14	Varies greatly in composition.
LARD OIL,	Obtained by pressing lard.	Olein.	·915	−4 to +10	290	19·3	13·8	Soluble in an equal weight of boiling alcohol. Gives a firm "elaidin."
TALLOW,	From the ox and sheep.	Stearin, palmitin, and olein.	(at $\frac{99°}{15\cdot5}$ C. ·856 to ·859)	33 to 47	283 to 290	19·3 to 19·8	13·8 to 14·2	Varies greatly in composition.
TALLOW OIL,	Obtained by pressing tallow.	Olein.	·916	0 to 6	288 to 292	19·2 to 19·4	13·7 to 13·9	Much resembles lard oil.
WHALE OIL,	Blubber of *Balæna mysticetus* and various allied species.	Olein (Valerin).	·920 to ·931	..	250 to 296	18·9 to 22·4	13·5 to 16	Yellow or brown colour; disagreeable fishy smell. Gives a pasty "elaidin."
B. Of Vegetable Origin.								
CASTOR OIL,	Seeds of *Ricinus communis*.	Ricinolein.	·958 to ·970	− 18	302 to 319	17·6 to 18·1	12·6 to 13·1	Very viscous. Readily soluble in alcohol.
COCOA-NUT OIL,	Nuts of *Cocos nucifera* and butyracea.	Laurin, palmitin, and stearin.	(at $\frac{99°}{15\cdot5}$ C. ·868 to ·874)	14 to 23	209 to 228	24·6 to 26·8	17·6 to 19·2	Consistency of butter. Used in "marine" soaps.
COTTONSEED OIL,	Seed of *Gossypium barbadense* and allied species.	Olein and stearin (linolein).	·916 to ·930	1 to 10	267 to 294	19·1 to 19·7	13·6 to 14·1	Gives a pasty "elaidin." Fatty acids melt at 38° C.

EARTH-NUT OIL,	Nuts of *Arachis hypogea.*	Olein, palmitin, arachidin.	·916 to ·922	− 5	289	19·3	13·8	Gives a firm "elaidin." Resembles olive oil, but contains glycerides of arachidic and hypogeic acids.
HEMPSEED OIL,	Seed of *Cannabis sativa.*	Linolein.	·925 to ·931	− 15 to − 28	290	19·3	13·8	Similar to linseed oil.
LINSEED OIL,	Seed of *Linum usitatissimum.*	Linolein.	·931 to ·937	− 20 to − 27	288 to 300	18·7 to 19·5	13·3 to 13·9	Remains liquid when treated with nitrous acid.
NIGER-SEED OIL,	Seed of *Guizotia oleifera.*	Linolein.	·924 to ·928	below − 9	268 to 295	to 19·4	13·5 to 13·8	Similar to linseed oil.
OLIVE OIL,	Fruit of *Olea Europœa.*	Olein.	·914 to ·917	− 6 to + 4	286 to 303	19 to 19·5	13·6 to 13·9	Gives a pale yellow solid "elaidin."
PALM OIL,	Fruit of *Avoira elais.*	Palmitin and olein.	·920 to ·945	20 to 36	277 to 286	19·6 to 20·2	14 to 14·4	Composition varies greatly; often contains much free palmitic acid.
RAPESEED OIL,	Seed of *Brassica sampestris,* &c.	Brassein.	·911 to ·917	− 6 to − 10	314 to 328	17 to 17·6	12·2 to 12·6	Gives a soft "elaidin."
SESAME OIL,	Seeds of *Sesamum indicum.*	Olein.	·921 to ·924	− 4 to − 6	292 to 2	18·9 to 19·2	13·6	Gives a pasty "elaidin."
SHEA BUTTER,	Seeds of *Bassia parkii.*	Stearin and olein.	·917	23 to 43	292 to 313	18·4	13·2	Resembles tallow.
OLEIC ACID OR "OLEINE,"	By pressing mixed fatty acids from tallow and palm oil (candles).	Oleic acid.	·887 to ·908	6 to 22	281 to 293	19·1 to 19·9	13·6 to 14·2	Varies greatly in composition; frequently contains glycerides as well as hydrocarbon oils.
RESIN OR COLOPHONY,	Residue from distillation of crude turpentine.	Abietic acid, &c.	1·04 to 1·10	135	290 to 330	17 to 19·3	12·2 13·8	Used only in conjunction with other oils and fats, for yellow household soaps and sometimes for soft soaps.

potash and oils containing principally olein, linolein, or ricinolein. Potash soaps are highly deliquescent. According to Lant Carpenter, 100 parts of potassium oleate, exposed to air, absorb 162 parts of water, and 100 parts of potassium palmitate absorb 35 parts, whereas 100 parts of dry sodium stearate absorb only $7\frac{1}{2}$ parts. These quantities, of course, are liable to vary according to the condition of the atmosphere, but they indicate comparative results.

Some soaps, notably those made with cocoa-nut oil, have a remarkable property of retaining a very high percentage of water (70 to 80 per cent.) and still remaining fairly hard.

Soaps are insoluble in solutions of alkaline salts, and also in strong solutions of caustic alkali; hence, in the process of manufacture, the potash or soda used must not be of more than a certain strength, otherwise the partially formed soap will be thrown out of solution. On the addition of common salt to a solution of soda soap the latter separates out as a curdy mass and rises to the surface. This property is utilised on the large scale for separating the soap from excess of alkali and impurities in the "lye" employed. The glycerin liberated by the decomposition of the fatty matter also remains in the alkaline solution. The operation is usually termed "salting out." For the production of a pure neutral "curd" soap the solution is run off, the soap dissolved in a fresh quantity of water, and the operation of salting out repeated. When common salt is added to a solution of potash soap a double decomposition takes place, resulting in the production of a soda soap with formation of potassium chloride. In England potash soaps are not "salted out," hence "soft" soaps made with neutral oils and fats invariably contain glycerin, and usually excess of alkali. In some parts of the Continent where potassium chloride is abundant this salt is used for "salting out" in the production of a neutral potash soap.

For details of manufacture, works such as W. Lant Carpenter's *Soap, Candles, &c.*, Alder Wright's *Oils, Fats, Waxes, &c.*, and Richardson and Watt's *Chemical Technology* should be consulted. We shall only give here a brief outline.

Dr. C. R. Alder Wright, F.R.S.,[*] discusses the subject of soap manufacture with special reference to the objectionable effects of excess of alkalinity in soaps, and suggests a novel process (mentioned below) for removing these disadvantages.

The many varieties of soap may be conveniently classed into three leading divisions, according to the way in which the separation of glycerin and fatty acids is accomplished.

[*] *Journ. Soc. Dyers and Col.*, 1886, p. 17.

I. Soaps prepared from fatty acids by direct addition of alkalies thereto, the separation of glycerin from fatty acid having been previously accomplished — *e.g.*, soaps made from the fluid fatty acids of the candle maker. These soaps are necessarily devoid of glycerin.

II. Soaps made by treating fats and oils with alkalies along with limited amounts of water in such fashion that saponification is effected, and the whole mass finally allowed to solidify without the separation of the glycerin from the soap formed. Such soaps always contain glycerin.

III. Soaps made by boiling together fatty matters and alkaline solutions of weaker strength than those used for the second class; and finally separating the soap produced from the glycerin by rendering the soap insoluble in the aqueous fluid which contains the glycerin dissolved, and mechanically drawing off separately the two products. Here the insolubility is usually brought about by "salting out"—*i.e.*, adding salt or brine to the mass when the saponification is complete or nearly so. Like soaps of the first class, these soaps are devoid of any notable amount of glycerin.

Besides these three main groups there are other varieties made by combinations of processes belonging to the above groups; and, among these, resin soap may be more particularly mentioned, made by uniting resinous acids and alkalies together by treatment similar to that of the first group, save that the resins are used instead of the candle makers' fluid acids (red oils or olein); and then blending the products thus obtained with a boiled soap, usually made by a process of the third class, or by combined methods equivalent to so doing.

Method I.—Soaps of the first group are usually prepared by making a caustic alkaline lye of proper strength and mixing together definite quantities of this and of the fatty acids, and then allowing to cool and solidify as a whole. It is obvious that unless great care is taken in exactly proportioning the two ingredients, the resulting mass will contain an excess of either alkali or acid. Soaps of this class are generally made with a slight excess of alkali. Similar remarks also apply to soap made by processes of the second class. Large quantities of soap are made by the above method from "olein" and potassium or sodium carbonate for washing raw wool, yarn, and cloth.

A solution of potash soap, suitable for washing wool, may be readily obtained by boiling 100 lbs. of "olein" and 25 to 30 lbs. of pure potassium carbonate (or an equivalent amount of commercial pearl ashes) with about 100 gallons of water in a large iron tank; 25 lbs. of potassium carbonate are required to

produce a neutral soap, but for most kinds of work at least 30 lbs. may be used with advantage. On account of its cheapness, soda soap, although inferior to potash soap (see below), is generally employed for washing wool and woollen fabrics—especially for low-class goods. To produce a neutral soda soap with 100 lbs. of "olein," about 19 lbs. of pure sodium carbonate are required, but in practice, at least, 25 lbs. are usually taken.

"Olein," in addition to its direct use, is also largely employed in conjunction with other oils and fats for making soaps by the third method.

Method II.—Three principal sub-divisions of this class may be mentioned :—1st, The temperature is kept as low as possible during the action of the alkali on the fatty matter, and no boiling down is effected (so-called "cold process" largely used for per-fumers' toilet soaps); 2nd, The action takes place at boiling heat in open vessels, causing evaporation—*e.g.*, in the manufacture of soft soap; or 3rd, Saponification is effected in closed vessels under pressure, or in open vessels at temperatures above the boiling point; but in all three cases excess or deficiency of alkali may occur through want of due care. In practice the latter is esteemed the worse evil of the two, so that soap made by any of these processes is generally made to contain a more or less considerable surplus of alkali over and above that equivalent to the fatty matter employed. This defect is more likely to occur in cold process soaps than in the others.

Considerable quantities of soap prepared by the "cold process" are used for scouring purposes in the textile industries.

W. J. Menzies recommends the following quantities for making a good potash soap by the "cold process" for washing wool :—50 lbs. of Greenbank caustic potash (the alkali must be pure and free from carbonate) are dissolved in 5 gallons of water and allowed to cool. The solution is then gradually poured into a vessel containing 200 lbs. of Gallipoli olive oil with constant stirring with a flat wooden stirrer about 3 inches broad. The stirring is continued until the oil and potash have become thoroughly mixed, when the vessel is covered and put in a warm place for a day or two. The combination between the oil and alkali commences a short time after mixing, and is accompanied by a considerable elevation of temperature.

The above quantities give an almost neutral soap. For anything but the finest work the amount of oil may be reduced to 180 lbs. It is preferable, however, to make a neutral soap and afterwards treat it with refined pearl ashes (potassium carbonate) in the pro-portion of about 1 to 3 per cent. In place of olive oil, cottonseed oil, &c., or mixtures of these, may, of course, be used. If it is

desired to give the appearance of "figs" to the soap, a little tallow is used in place of a portion of the oil. A neutral hard soda soap may be obtained in the following manner :—150 lbs. of tallow, palm oil, or cocoa-nut oil are melted and brought to a temperature not exceeding 40° C., and a solution of 20 lbs. of pure caustic soda dissolved in 75 lbs. of water at a temperature of about 22° C. gradually added during constant stirring. The mixture is then poured into a soap frame, covered up and put in a warm place for a few days.

Method III.—Soaps of the third class are those most largely used for industrial opera-tions, although a very considerable quantity of soft (potash) soap made by methods of the second kind is also produced principally for use in the woollen industries.

Soft soaps are usually made by boiling olive, cottonseed, linseed, rape seed, hemp seed, and other oils, or mixtures of these, with caustic potash lye. The oil is run into the pan to the extent of one-fourth of its capacity, and the requisite amount of a solu-tion of caustic potash (containing a little carbonate) of specific gravity 1·065 to 1·08 (13° to 16° Tw.) added at the same time. The mass is boiled for some hours until saponification has taken place, the completion being determined by the appearance which small samples present when allowed to cool on glass plates. If more alkali is required, a solution of caustic potash, ranging from 1·12 to 1·2 specific gravity (24° to 40° Tw.), is gradually and cautiously added, and the boiling continued. The direct steam (if used) is then turned off, and a portion of the water evaporated by boiling with fire or "close" steam only. The finished soap is then run into casks while still hot.

"Hydrated" soda soaps are made in much the same manner as "soft" potash soaps, using an equivalent amount of caustic soda lye in place of caustic potash. The fatty matters used comprise tallow, palm oil, cocoa-nut oil, lard, oleic acid, castor oil, olive oil, &c. The amount of uncombined alkali in such soap, although varying greatly, is usually much less than in soft potash soaps. Soaps of this class containing an excess of alkali are largely used for scouring purposes. Others which are neutral, or contain an excess of fatty matter, are extensively used as "soft-eners" for treating dyed cotton goods. For this purpose palm oil is the principal fatty matter employed.

Hard soaps made by open-pan boiling, where the glycerin is eliminated by "salting out," are manufactured on an enormous scale. According to Lant Carpenter, probably 90 per cent. of the total soap produced in English-speaking countries is made in this way. The principal varieties are known as curd, mottled, and yellow. Almost all kinds

of fatty matter are used, and for "yellow household" soaps resin is also largely employed, along with tallow, palm oil, and other fats.

Curd soaps should be free from resin. They are of great importance for milling and scouring dyed fabrics.

Some consider that, other things being equal, a soda soap exerts a far more marked injurious action on wool than a potash soap; the "suint," or wool grease, of the fleece is a kind of natural soap, and is remarkable in this respect that it scarcely contains any soda, potash being almost the sole alkaline constituent. Accordingly, for wool scouring, potash soaps free from soda are usually preferred; but on the other hand a notable amount of injury to the wool may be brought about if the soap contains any considerable excess of alkali, and more especially if resinate or silicate of potash be also present. Fusel oil has been used as a cleansing agent for wool, and comparative tests demonstrated that a larger yield of cleaned wool was obtained by its use than with a similar batch of wool treated in the ordinary way. A microscopic examination of wool which has been treated with soap shows that the edges of the nests or thimbles (with which a wool fibre may be compared) have been split, and appear more or less shrivelled, and the more alkaline the soap the more the fibre is attacked. It is obvious that the more free from surplus uncombined alkali the potash soap is made, the more suitable it is for this special purpose; in fact, when the quantity of surplus alkali becomes moderately marked, less injury is effected by the use of a soda soap *free from surplus alkali* than by the alkaline potash soap, although a neutral potash soap, of course, produces still less injury. The employment of certain salts of ammonia for removing the excess of alkali from soaps depends on the circumstance that potash and soda and the carbonates of these metals, possess the property of displacing ammonia from its compounds with acids. For example, ammonium chloride combines with sodium carbonate to form sodium chloride and ammonium carbonate; consequently, if ammonium chloride be added to a soap containing free sodium carbonate, the result is a neutral soap, together with a volatile alkali, which has no injurious effect on wool.

The process of effecting the elimination of surplus alkali may be applied to soft soaps (freed as far as possible from any large excess of alkali by exercising due care in manufacture) by thoroughly crutching in an appropriate amount of the ammoniacal compound before barrelling the soap. All soaps treated in this way emit a smell of ammonia on opening the barrels. Soaps de-alkalised by this method are well suited for use where an article devoid of excess of free alkali is of importance.

Similar remarks apply to "oil" soaps for fulling purposes made from oleic acid, &c., the de-alkalising agent being crutched in as late as possible consistent with due admixture, and the mass allowed to solidify.

For certain purposes, and more particularly for clearing printed calicoes after dyeing, and similar operations carried out with other cotton goods, an excess of alkali amounting to only 0·1 or 0·2 per cent. is injurious, certain colours being more prone to alteration under such treatment than others; accordingly, the calico printer requires for such purposes, a soap as nearly approaching to absolute freedom from excess of alkali as possible. This result is readily attainable by treating the soap before solidifying in the frames with the proper amount of ammoniacal salt, the minute amount of ammonia retained in the bars, after cutting and stacking, exerts a very far less injurious action upon sensitive colours than the corresponding quantity of fixed alkali.

According to Thorp Whitaker,[*] in many cases the material (especially wool), after dyeing, contains a considerable amount of free acid, and if a perfectly neutral soap were used, a portion would be decomposed and free fatty acids deposited on the fibre. In such cases, therefore, a soap containing $\frac{1}{4}$ per cent. of free alkaline carbonate, if properly used, will not injure the colours.

Rawson has tabulated the results of a number of analyses of manufacturers' soaps which are used in scouring, milling, and as softeners (see p. 289).

ANALYSIS.

In many cases of soap analysis it is merely necessary to estimate the amount of *water*, *fatty acids*, and *total alkali*. It is frequently of importance, however, to determine the amount of combined and free alkali as well as uncombined fat.

A complete analysis would include the following determinations:—Water, uncombined fat, combined fatty acids (calculated as anhydrides), glycerin, resin, combined alkali, caustic alkali, sodium or potassium carbonate, chloride, sulphate and silicate, insoluble matter (clay, sand, oxide of iron, &c.).

In addition to these determinations, it is often necessary to make an examination of the fatty acids in order to ascertain the kind of oils and fats which have been used in manufacturing the soap.

In taking portions for analysis, sections should be cut across the centre of a bar in the case of hard soaps, and the outer portion

[*] *Journ. Soc. Dyers and Col.*, 1887, p. 41.

of a soft soap should be removed. The different weighings should all be made at one time in order to guard against any irregularity caused by the sample losing water.

Water.—The usual method is to weigh about 3 grms. in the form of thin shavings in a porcelain basin, and dry in an air bath at a temperature of 110° C. until the weight is constant. In the case of soft potash soap, a small glass rod should be weighed with the dish so that the soap may be stirred from time to time. Hard soaps require about four hours, but soft soaps frequently require a much longer time.

Watson Smith * recommends the following modification :—From 5 to 10 grms. of soap in thin shavings are weighed into a counterpoised crucible containing a piece of glass rod, flattened at the upper end and rough and jagged at the lower extremity. The crucible is placed on a sand bath, which is gently heated by a Bunsen burner ; the contents being continually stirred and turned

* *Journ. Soc. Dyers and Col.*, 1884, p. 31.

Potash Soaps for Washing Raw Wool, &c.

In 100 parts.	Made from Olive and Cottonseed Oils.	Made from Olive Oil and Tallow.	Made from Olive Oil.	Made from Cottonseed Oil.	Source Unknown.
Water,	42·20	37·10	48·75	41·78	45·95
Combined alkali (K_2O),	9·20	10·08	7·32	9·05	7·78
Fatty anhydrides,	43·78	47·50	38·37	43·82	40·36
Potassium hydrate,	0·45	0·28	0·22	0·15	} 1·50
Potassium carbonate,	0·82	1·58	2·05	1·40	
Glycerin, &c. (by diff.),	3·55	3·46	3·29	3·80	4·41
Melting point of fatty acids, °C.,	29	31	26	37	32

Soda Soaps.

	For Milling Cloth.			For Scouring Purposes.		
	Made from Tallow.	Made from Tallow and Palm Oil.	Made from Tallow, Cottonseed Oil, &c.	Made from Palm Oil, Whale Oil, &c.	Made from Olive Oil.	Made from Tallow, Cottonseed Oil, &c.
Water,	26·73	29·53	23·25	25·38	29·56	18·55
Combined soda (Na_2O),	7·98	7·78	8·57	7·31	7·07	7·98
Sodium carbonate,	0·18	0·26	0·12	0·75	0·35	0·42
Fatty acids,	67·22	64·05	69·50	65·40	64·11	72·60
Melting point of fatty acids, °C.,	44	40	38	36	23	37

"Softening Soaps" (Soda).
Made Principally from Palm Oil or Palm Oil with Oleic Acid.

	A.	B.	C.	D.	E.
Water,	66·80	64·40	32·50	28·05	67·50
Combined soda (Na_2O),	3·15	3·40	7·20	7·50	1·05
Fatty anhydrides,	25·95	30·50	54·35	59·15	7·25
Free fat,	1·05	0·50	2·20	1·25	22·86
Sodium carbonate,	0·15	0·10	0·25	0·20	} 1·34
Glycerin, &c. (by diff.),	2·90	1·10	3·50	3·85	

over with the glass rod. The end of the operation is ascertained by removing the lamp and holding a watch-glass over the crucible. When no more moisture becomes deposited on the glass, the crucible is placed in a desiccator, cooled, and weighed. Even if the soap burns a little, so penetrating is the odour of burnt soap that it will be immediately detected, and the loss thus caused is usually quite inappreciable. The operation can be performed in about twenty minutes. With potash soaps and others containing glycerin the results are not satisfactory, since it is difficult to ascertain exactly when all the water is driven off.

Total Alkali.—5 grms. of soap are dissolved in about 200 c.c. of hot water, and with either methyl orange or cochineal as indicator, titrated with $\frac{N}{5}$ sulphuric acid, each c.c. of which corresponds to 0·0062 grm. Na$_2$O, or 0·0094 grm. K$_2$O. The fatty acids set at liberty have no action upon either of these indicators.

If the amount of *potash* be required when both potash and soda are present, a given weight of soap is decomposed with hydrochloric acids and the filtered solution treated with platinum chloride (*v.* p. 263).

Uncombined Alkali.—This may exist in a soap either as *caustic* or *carbonate*, or both. About 3 grms. in fine shavings are weighed, and dried in a water oven for about two hours. A water oven is preferable to an ordinary air-bath, since any caustic alkali which may be present is less liable to be converted into carbonate during the process of drying. In order to avoid this source of error altogether it is necessary to use a specially constructed bath arranged to prevent access of carbon dioxide. After drying, the soap is placed in a ribbed filter paper and introduced into a Soxhlet tube, the lower end of which is connected to a small wide-mouthed flask containing pure alcohol, to which has been added a few drops of phenolphthaleïn and sufficient caustic potash (a drop or two of $\frac{N}{10}$ KOH will usually suffice) to render the liquid faintly pink. The upper extremity of the Soxhlet tube is connected with an inverted Liebig's condenser, and the small flask immersed to the neck in water, which is kept at or near the boiling point. The alcohol is volatilised and the vapour condensed in the Soxhlet tube. A portion of the soap and caustic alkali (if present) dissolves, and the solution flows over into the flask by means of the small syphon. The operation must be continued until the whole of the soap has dissolved. The time required varies considerably according to the nature of the soap and the rate at which the alcohol distils. From two to four hours will be required on an average. The alcoholic solution contains the pure soap, and any glycerin and caustic alkali which may be present. If any caustic alkali has been extracted the solution will be pink. It is titrated with $\frac{N}{10}$ acid until the colour disappears. Each c.c. = 0·004 grm. NaOH, or 0·0056 grm. KOH. The residue insoluble in alcohol may contain, in addition to sodium or potassium carbonate, chlorides, sulphates, silicates, and insoluble matter. It is dissolved in water and titrated with $\frac{N}{10}$ sulphuric acid and methyl orange. Each c.c. = 0·0053 grm. Na$_2$CO$_3$, or 0·0069 grm. K$_2$CO$_3$. For a more complete analysis of the residue see Dr. Leeds' scheme (p. 291).

Combined Alkali.—The alkali existing as carbonate (also silicate, if present) and caustic is subtracted from the total alkali, when the difference gives the amount of alkali combined with fatty acids as soap. The combined alkali may also be determined in the alcoholic extract after neutralising any free caustic alkali or free fatty acid (which will have decolorised the solution) with acid or alkali, as the case may be. Water is added to the soap solution, which, with a few drops of methyl orange, is titrated with standard acid. The acid thus consumed corresponds to combined alkali.

The combined alkali may also be calculated from the amount of standard alcoholic potash required to neutralise the liberated fatty acids in the method described below. The total alkali having been determined, this method affords a means of estimating the uncombined alkali by difference.

Fatty Acids.—(*a*) In a careful determination of all the other constituents of a soap, the fatty acids may conveniently and with accuracy be ascertained *by difference*, as recommended by Watson Smith.*

(*b*) About 3 grms. of soap are dissolved in 60 c.c. of water and introduced into a stoppered separator of 200 c.c. capacity. The soap is decomposed with a slight excess of hydrochloric acid, and, when cold, about 50 c.c. of ether added, and the whole well shaken. When the two liquids have separated, the acid solution is run off into a second similar separator and extracted twice more with successive portions of 25 c.c. ether. The ethereal extracts are mixed and washed by shaking with three portions of 25 c.c. of cold distilled water. The solution of fatty acids is then carefully poured into a small weighed wide-mouthed flask, and the separator well rinsed out with pure ether. The ether is distilled off, and in order to get rid of water (usually present in the residue) a little strong alcohol is added, and the flask heated on the water bath until the alcohol has volatilised. The flask is then heated in the water-oven and weighed. By this process, the weight

* *Journ. Soc. Dyers and Col.*, 1884, p. 31.

Weigh out 5 grms.   Dry at 110° C.   Loss corresponds to water.

Treat with Petroleum Ether.

Extract is uncombined fat. Dry at 100° C. and weigh.

Residue is soap and mineral constituents. | Treat with alcohol.

Extract is soap (fatty anhydride, resin, and combined alkali), glycerin, and free alkali. Add 3 drops of phenolphthalein. If necessary, titrate with normal H_2SO_4.

Add a large excess of water and boil off the alcohol. Decompose with excess of normal H_2SO_4. Boil, filter, wash.

RESIDUE.—Fatty acids and resin. Dry at 110° C. and weigh.

Dissolve an aliquot part in 20 c.c. strong alcohol, and, using phenolphthalein as an indicator, saponify with soda in slight excess.

Boil, cool, and add ether to 100 c.c.

Decompose with $AgNO_3$ by adding in fine powder, shake well for ten minutes, and allow to settle.

Precipitate is stearate, palmitate, and oleate of silver.

SOLUTION.—Resinate of silver. Filter 50 c.c. from the total 100 c.c. Decompose with 20 c.c. HCl (1 : 20). Allow the AgCl to settle, and evaporate an aliquot part of the ethereal solution in a tared dish. Dry at 100° C. and weigh. After applying correction for oleic acid, the weight corresponds to the resin. This weight subtracted from the combined weight of fatty acid and resin gives the fatty acids.

FILTRATE.—Combined soda and glycerin. Titrate with normal NaOH.

H_2SO_4 used corresponds to free alkali. Calculate as NaOH.

After titration, evaporate to dryness on the water-bath.

H_2SO_4 used corresponds to combined soda in soap. Calculate as Na_2O.

Treat with absolute alcohol.

Evaporate the alcoholic solution to dryness in a tared dish and weigh as glycerin.

RESIDUE.—Na_2CO_3, NaCl, Na_2SO_4, sodium silicate, starch, and insoluble residue. Wash with 60 c.c. water.

FILTRATE.—Na_2CO_3, NaCl, Na_2SO_4, and sodium silicate. Divide into four equal parts.

Na_2CO_3. Titrate with normal H_2SO_4, and calculate as Na_2CO_3.

NaCl. Titrate with $AgNO_3$, or weigh as AgCl. Calculate as NaCl.

Na_2SO_4. Weigh as $BaSO_4$. Calculate as Na_2SO_4.

Sodium silicate. Decompose with HCl and determine soda combined in silicate and silica.

RESIDUE.—Starch and insoluble residue. Dry the filter and weigh. The weight is the starch and insoluble residue.

STARCH.—Convert the starch into $C_6H_{10}O_5$. Titrate with Fehling's solution.

Subtract the weight of starch found, and the difference is the insoluble mineral constituents.

obtained will, of course, include any uncombined fat or unsaponifiable oil, if present. In practice it is not often necessary to estimate the last-mentioned substances, but, if required, they are determined as below, and their amount deducted from the weight of fatty acids obtained as above. Previous to the determination of fatty acids, extraction of the dried soap with petroleum ether will remove free fat and unsaponifiable oil.

Free Fat and Unsaponifiable Oil. — This may be determined by extracting the dried soap in a Soxhlet tube with petroleum ether (previously distilled on the water-bath, the non-volatile residue being rejected), the residue, after volatilisation in the solvent, being weighed. A preferable plan, recommended by Allen, consists in dissolving the soap in water and shaking the solution with ether in a separator. After the liquids have separated (which frequently takes a considerable time), the aqueous solution of soap is run off into another separator and shaken up a second time with ether, unless the amount of unsaponified matter is very small. The ethereal solutions are combined, washed with water, poured into a flask, and the ether volatilised. Soap being slightly soluble in ether, may be present in the residue. Digesting with cold petroleum ether in small quantity, and subsequent filtration into a small wide-mouthed flask, distillation of the solvent and weighing the residue will rectify any error from this source. If this precaution be taken, it is allowable to add to the mixture of soap and ether during the first extraction, a little alcohol, which assists materially in causing a quicker separation of the aqueous and ethereal layers.

Examination of Fatty Matter in Soap. — In the analysis of soap it is frequently desirable to ascertain what kind of oils and fats have been used in its manufacture. This is the most difficult part of the examination. Much information may generally be obtained from a determination of the saponification equivalent, the specific gravity, and the melting and solidifying points of the fatty acids of the soap, which may be liberated by the addition of hydrochloric acid. A few brief descriptions only will be here given. For fuller particulars, reference should be made to such works as Allen's *Commercial Organic Analysis*, vol. ii.

About 40 grms. of soap are dissolved in water in a separator, and the fatty acids liberated by means of hydrochloric acid. The fatty acids are separated by agitating with ether, washing the ethereal solution with water, evaporating the ether, and drying the residue in the water oven.

Saponification Equivalent. — About 5 grms. of the fatty acids are dissolved in 60 c.c. of hot *neutral* alcohol, and, with phenolphthaleïn

as indicator, titrated with $\frac{N}{2}$ alcoholic potash. The weight in milligrams of the fatty acids taken, divided by half the number of c.c. of $\frac{N}{2}$ KOH required, gives the saponification equivalent.

Specific gravity is best determined at 100° C. in a small Sprengel tube of a capacity of about 7 c.c. The weight of the dry tube and that of water contained in it at 15·5° C. are first ascertained. The tube is then filled with the melted fatty acid and placed in the mouth of a conical flask containing water, which is kept briskly boiling. The oil expands, and the excess flows out in drops from the capillary orifice. When the expansion ceases, any oil adhering to the orifice is carefully removed by means of filter paper, the tube removed, dried, cooled, and weighed. The weight thus obtained divided by the weight of water required to fill the tube at 15·5° C. will give the density or specific gravity of the fatty acids at 100° C. compared with water at 15·5° C. as unity.

The melting point of the fatty acids may be conveniently observed in the following manner :—A piece of quill-tubing is drawn out into a long capillary tube, which is cut up into lengths of about 3 inches. One of these is dipped into the molten fatty acid, and a *small* quantity, occupying about a quarter of an inch, drawn up and allowed to solidify. After standing half an hour the melting point may be observed. As fats after being melted do not regain their original melting point for a considerable time, it is best to leave the tube overnight, and then proceed with the determination.

The tube is attached to the stem of a thermometer by means of a small india-rubber ring (a small piece cut off a piece of india-rubber tubing answers well) in such a manner that the fatty acid is close to the centre of the bulb. The thermometer with the tube is immersed in a small beaker filled with water, the beaker itself being immersed in a conical flask filled with water. A Bunsen flame is placed under the flask, and the mercury column and the substance carefully watched. The temperature should not be allowed to rise more than $\frac{1}{2}$° C. per minute. When the fatty acid melts, the temperature is at once observed and recorded.

The solidifying point of the fatty acids is best determined as described by Allen in the following manner :—A test tube, about 5 inches in length and $\frac{3}{4}$ inch in diameter, is fitted with a ring or collar of cork, by which it is fixed in the mouth of an empty flask. The melted fatty acid is poured into the warmed tube till it is about two-thirds filled, and a delicate thermometer, previously warmed, is suspended freely in the liquid, the bulb being wholly immersed. When the

fatty acids begin to solidify at the bottom of the tube, the thermometer must be attentively observed. The contents of the tube are then slowly stirred, by giving the thermometer a circular movement, first three times to the right then thrice to the left. The first effect of the agitation is to cause the mercury column to fall slightly, but subsequently a sensible rise takes place, and the mercury remains stationary for at least two minutes. The temperature thus indicated is the solidifying point of the substance, and the results obtained are remarkably constant. The following table, chiefly compiled from figures in Allen's *Commercial Organic Analysis*, will be found useful in drawing conclusions from data obtained by the above methods :—

Source of Fatty Acids.	Saponification Equivalent or Combining Weight.	Specific Gravity at 98° to 99° C. compared with Water at 15·5°.	Melting Point. ° C.	Solidifying Point. ° C.
Olive oil,	279	·843	26	21
Cottonseed oil,	277	·847	35	32 to 37
Rape oil,	321	·844	19·5	12 ,, 18
Linseed oil,	307	·861	20	18 ,, 20
Tallow,	277	·857	45	43 ,, 58
Palm oil,	270	·837	45	36 ,, 45
Cocoa-nut oil,	200	·835	24	20 ,, 25

Glycerin.—In Leeds' scheme (p. 291) glycerin is determined gravimetrically, but at 100° C. glycerin volatilises somewhat freely, and the results are consequently too low. In the absence of sugar, it may be conveniently estimated by Benedikt and Zsigmondy's process,[*] originally suggested by Wanklyn, and also investigated by Fox. The method is based upon the fact that when glycerin is oxidised in alkaline solution with potassium permanganate, it is converted into oxalic acid, carbon dioxide, and water—

$$C_3H_5(OH)_3 + 3O_2$$
$$= C_2H_2O_4 + CO_2 + 3H_2O.$$
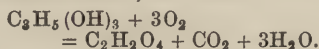
In the absence of sugar this method may be employed directly; if sugar be present it must first be removed by means of lime. 10 grms. of soap are dissolved in water and decomposed with dilute hydrochloric acid. The solution freed from fatty acids is diluted to 400 c.c., and made strongly alkaline with 15 grms. of solid caustic potash. A strong solution of potassium permanganate is added until the colour of the liquid changes from green to bluish-black. The mixture is boiled for an hour in a porcelain basin, when the excess of potassium permanganate is destroyed by the addition of a strong solution of sodium sulphite, and the liquid filtered. The filtrate is acidulated with acetic acid and boiled, and the oxalic acid present precipitated by calcium acetate. The precipitate of calcium oxalate thus obtained may contain silica and calcium sulphate, and cannot therefore be weighed as carbonate. The precipitate may be ignited, and the lime estimated by titration with standard nitric acid and caustic soda; or, preferably, the calcium oxalate is dissolved direct in dilute sulphuric acid, and

the oxalic acid estimated by titration with $\frac{N}{10}$ permanganate, as on p. 255. 56 parts of CaO, or 126 parts of $C_2H_2O_4$, $2H_2O$ correspond to 92 parts of glycerin.

Resin.—E. Twitchell[*] recommends the following process, which gives satisfactory results :—2 to 3 grms. of fatty and resin acids (obtained by decomposing soap with dilute HCl) are dissolved in ten times their volume of absolute alcohol in a flask, and dry hydrochloric acid gas passed through in a moderate stream. The flask is set in a vessel of water during the operation in order to keep it cool. The hydrochloric acid is rapidly absorbed, and after about forty minutes the ethers of the fatty acids separate and float on the surface. The flask is removed and allowed to stand half an hour longer, to ensure a complete combination of the alcohol and fatty acids. The liquid is diluted with 5 volumes of water, and boiled until the acid solution is clear, the ethers, with resin acids in solution, floating on the top. On cooling, some light petroleum ether is added, and the whole transferred to a separator. The acid solution is run off, and the petroleum ether solution (about 50 c.c. in volume) washed with water. A solution of 0·5 grm. of solid caustic potash in 5 c.c. of alcohol and 50 c.c. of water is poured into the separator, and the whole agitated. The resin acids are thus saponified, and the ethers of the fatty acids remain in the naphtha. The solution of resin soap is run off and decomposed by means of hydrochloric acid, the resin collected, dried, and weighed. Instead of weighing the resin it may be determined volumetrically by means of standard alkali. In this case, ether is used instead of

[*] *Journ. Soc. Dyers and Col.*, 1885, p. 245.

[*] *Journ. Anal. Chem.*, 1891, p. 379.

petroleum ether, and the washing with water must be continued until the wash water is no longer acid. 50 c.c. of neutral alcohol are then added to the ethereal solution of resin and ethers in the separator, and with phenolphthaleïn as indicator, titrated with standard potash or soda. The ethers of the fatty acids, under these conditions, are not affected by the alkali. The combining weight or saponification equivalent of resin acids is taken at 346.

The scouring value of soap is sometimes determined by means of a standard solution of calcium chloride. This solution (1·11 grm. $CaCl_2$ per litre) is prepared as described for determining the hardness of water (*v.* WATER). 5 grms. of the soap are dissolved in 300 c.c. of 90 per cent. alcohol, and diluted to 500 c.c. with water. The operation is performed in exactly the same manner as in estimating the hardness of water. 10 c.c. of the calcium chloride solution are mixed with 60 c.c. of distilled water and titrated with the soap solution, until a permanent lather is obtained. When two or more samples of soap are treated in this manner, the relative scouring value of the samples is inversely proportional to the number of c.c. consumed. The results are only approximately correct.

For further information on this subject a paper on " The Water-softening (or so-called ' scouring ') Power of Soaps," by F. W. Richardson and A. Jaffe (*Journ. Soc. Chem.*, 1899, p. 989), may be consulted.

SODA ASH *v.* SODIUM CARBONATE.

SODA CRYSTALS *v.* SODIUM CARBONATE.

SODIUM, Na = 23. Sodium occurs combined as the chloride in rock salt and in sea-water, as the nitrate in Chili saltpetre ($NaNO_3$), in the form of sulphate (Glauber's salt, $Na_2SO_4, 10H_2O$), and in many minerals combined with silica.

Preparation. — The metal is obtained by heating a mixture of calcined sodium carbonate, lime, and coal in small iron retorts, the vapours being condensed in flat iron receivers and the metal collected under rock oil.

Properties. — The metal is soft, and when freshly cut has a silvery metallic lustre. It quickly tarnishes on exposure to air, forming oxide of sodium, and eventually absorbing carbon dioxide, sodium carbonate being produced.

Sodium decomposes water, with liberation of hydrogen and formation of caustic soda solution—

$$Na + H_2O = NaOH + H.$$
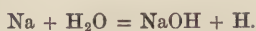
The compounds of sodium are widely distributed in nature, and many of them are manufactured on the large scale in enormous quantities.

SODIUM ACETATE, $CH_3.COONa + 3H_2O$. *Acetate of soda.*

Preparation. — This salt is formed by treating sodium carbonate with dilute acetic or pyroligneous acid, evaporating and crystallising. On adding sodium sulphate to calcium acetate solution, sodium acetate is produced and calcium sulphate is precipitated. After filtration the clear liquid is crystallised.

Properties. — Sodium acetate forms monoclinic crystals which dissolve in about 3 parts of cold water. The crystals melt in their water of crystallisation at 75° C., and become anhydrous at 100° C.

Sodium acetate is employed in the manufacture of acetic acid. It is also used in the preparation of diazo compounds in developing azo colours on the fibre, as it forms in the presence of mineral acids the sodium salt of the particular acid employed, and free acetic acid which does not injure the fibre or affect the colours.

The impurities in sodium acetate are sulphates, chlorides, and carbonates of calcium and sodium.

Analysis. — The *acetic acid* may be estimated by distillation with phosphoric acid (*v.* CALCIUM ACETATE).

The amount of *sulphate* present is determined by acidifying with hydrochloric acid and adding barium chloride to a solution of the salt. The precipitated barium sulphate is filtered, dried, ignited, and weighed, as described under standard sulphuric acid (*v.* ACIDIMETRY).

The percentage of *chlorine* is ascertained by dissolving a portion of the sodium acetate in water, acidifying with a few drops of nitric acid, boiling the solution and precipitating the halogen as silver chloride by adding silver nitrate. After filtration, the silver chloride is dried, detached from the filter, and just fused over a low Bunsen flame. The filter paper is incinerated separately and weighed. The latter addition to the weight of the crucible is filter ash and metallic silver, which must be calculated to AgCl, and added to the main portion of the precipitate.

The presence of *calcium* may be detected by adding a solution of ammonia and ammonium oxalate to a portion of the salt dissolved in water, a white precipitate of calcium oxalate being produced.

SODIUM ALUMINATE *v.* ALUMINIUM (ALUMINATE OF SODA).

SODIUM AMALGAM. An alloy of sodium and mercury.

SODIUM ARSENATE, $Na_2HAsO_4 + 12H_2O$, *Arsenate of soda, " Dung salt."* Sodium arsenate is prepared by decomposing sodium carbonate with arsenious oxide, evaporating to dryness with sodium nitrate, and heating the residue.

The commercial product is a mixture of this salt and sodium di-hydrogen arsenate, $NaH_2AsO_4 + H_2O$, and contains 30 to 60 per cent. of arsenic acid (As_2O_5). Common salt is often present in quantity. The substance occurs in commerce as crystals, in white lumps, or as a solution.

It is used to a large extent by calico printers as a substitute for cow-dung in the so-called "dunging" or "cleansing" operation. In this process the iron and aluminium mordants are converted into insoluble arsenates and are thus fixed. The excess of these mordants used in printing is also thus made insoluble and prevented from being absorbed by the portions of the fibre which it is intended should remain white. In yarn dyeing it affects the hands of all those who handle the goods, owing to its poisonous properties. Traces of arsenic may remain in the finished goods, and may cause the wearers of such articles to suffer from poisoning, though authentic cases are very rare. The waste water from such dye-baths will also contaminate the streams into which it is turned.

Analysis.—Arsenious acid, if present, is estimated by dissolving 2 grms. of the sample in water containing about 5 grms. of sodium carbonate, and diluting to 500 c.c. 100 c.c. ($= 0·2$ grm.) are withdrawn, neutralised with a little pure hydrochloric acid, 25 c.c. of a saturated solution of sodium bicarbonate added, and the liquid titrated with $\frac{N}{10}$ iodine.

1 c.c. $\frac{N}{10}$ iodine = 0·00495 grm. As_2O_3.

Commercial sodium arsenate sometimes contains 1 to 5 per cent. free As_2O_3.

Arsenic Acid.— Watson Smith * recommends the following method, worked out by J. Barnes :—2 grms. of the sample is dissolved in 100 c.c. of warm water in a flask of 500 c.c. capacity. A little sodium acetate is added to prevent any irregularity caused by sodium chloride which may possibly be present. A current of well washed sulphur dioxide is now passed through the solution until it smells of the gas. The liquid is then boiled until free from sulphur dioxide, allowed to cool, and diluted to 500 c.c. ; 50 c.c. of this solution ($= 0·2$ grm. of sample) are withdrawn and mixed with 25 c.c. of a saturated solution of sodium bicarbonate, and a little starch solution. The liquid is then titrated with $\frac{N}{10}$ iodine, each c.c. of which is equivalent to 0·00575 grm. of As_2O_5. From the percentage of As_2O_5 thus obtained the amount of arsenic, as As_2O_3, found by direct titration and calculated to As_2O_5, must be deducted. If the solution is very acid, after boiling off the sulphur dioxide, it is preferable to nearly

* *Journ. Soc. Dyers and Col.*, 1884, p. 34.

neutralise with normal sodium carbonate before adding the bicarbonate.

M'Kay has proposed a modification of Holthof's method, * the arsenate being not completely reduced to arsenite by operating in the manner described above. M'Kay mixes the arsenate solution with 20 c.c. of a solution of sulphurous acid, in a bottle provided with a well fitting ground-glass stopper, and capable of holding about 50 c.c. The stopper is firmly tied down with a piece of stout cord, and the bottle then placed in a water-bath, which is kept briskly boiling for one hour. The bottle is then removed from the bath, and. when nearly cold, opened and the contents rinsed into a flask, diluted to 150 c.c., and concentrated to one-half. On cooling, the liquid, free from sulphur dioxide, is diluted to a known bulk, and an aliquot part titrated with iodine substantially as above. M'Kay uses $\frac{N}{40}$ iodine. Holthof's original method consists in heating the arsenate solution with about 100 c.c. of sulphurous acid and the same quantity of water for about four hours on a water-bath, and then boiling down over a free flame to one-half the original volume. M'Kay finds this mode of procedure to give accurate results, and apparently the only advantage of his modification is a saving in time. In many cases, however, where a number of samples have to be examined, heating gently for four hours may be preferred to boiling under pressure for one hour.

Arsenic acid in sodium arsenate may also be determined by converting it into ammonium-magnesium arsenate, drying at 100° C. and weighing on a tared filter ; also by reduction with sulphur dioxide as above, conversion into arsenious sulphide (As_2S_3), and drying at 100°.

SODIUM BICHROMATE *v.* CHROMIUM TRIOXIDE.

SODIUM BISULPHITE, $NaHSO_3$. Sodium bisulphite forms easily soluble crystals, which gradually lose sulphur dioxide on exposure to the air, and oxidise slowly to sodium sulphate. The solution is prepared from sodium carbonate by passing a current of sulphur dioxide into the hot liquid until saturated.

$$Na_2CO_3 + 2SO_2 + H_2O = 2NaHSO_3 + CO_2.$$

The liquid keeps well in air-tight barrels. As sold it has a strength of 52 to 80° Tw. White crystals are deposited from concentrated solutions.

Sodium metabisulphite, $Na_2S_2O_5$, is a light yellow solid which resembles sodium bisulphite. Solutions of the bisulphite are almost colourless, and smell of sulphur dioxide. A liquid of 52 to 62° Tw. contains 20 to 23 per

* *Chem. News*, vol. liii., pp. 221, 223, 243.

cent. of SO_2. Sodium bisulphite is used as an antichlor, for bleaching silk and wool, for dissolving cerululëin and a few other colouring matters, and in the preparation of sodium hydrosulphite.

Analysis. — *Sulphur Dioxide*, SO_2. The best method of estimating the total amount of sulphur dioxide in sulphurous acid, sulphites, and bisulphites is by means of iodine, as described by Giles and Shearer.*

About 0·5 grm. of the sample (in the case of liquid sodium bisulphite it is better to take 10 c.c. and dilute to 500 c.c. with distilled water, which has recently been boiled and cooled) is weighed out and introduced at once into a known excess of decinormal iodine solution, and, after stirring, the excess of iodine is determined by a decinormal solution of sodium thiosulphate, as described under bleaching powder (*v.* CALCIUM CHLORO-HYPOCHLORITE).

The number of c.c. of $\frac{N}{10}$ thiosulphate are deducted from the number of c.c. of $\frac{N}{10}$ iodine taken, and the remainder calculated to sulphur dioxide.

1 c.c. of $\frac{N}{10}$ iodine = 0·0032 grm. of SO_2.

Example. — 10 c.c. liquid bisulphite of soda, specific gravity 1·25, were diluted with recently boiled and cooled water to 500 c.c. 20 c.c. of this solution (= 0·4 c.c. or 0·5 grm. of sample) were introduced into a beaker containing 35 c.c. of $\frac{N}{10}$ iodine. It was then found that 5·5 c.c. of $\frac{N}{10}$ thiosulphate were required.

$$\therefore \frac{0·0032 \times 20·5 \times 100}{0·5} = 18·88 \text{ per cent.}$$
of SO_2.

An excellent gravimetric method for estimating sulphur dioxide in sulphites is described by Giles and Shearer in the paper above-mentioned.

Indicators used in acidimetry are very differently affected by sulphurous acid and sulphites. With *phenolphthalëin*, for example, normal sodium sulphite, Na_2SO_3, reacts neutral, whereas the acid sulphite (bisulphite), $NaHSO_3$, is neutral to *litmus, cochineal,* and *methyl orange*. With litmus and cochineal the reaction is uncertain, but with methyl orange it is sharp and distinct. *Normal sulphites* may therefore be readily determined by titrating with normal sulphuric acid and methyl orange.

Free sulphurous acid and sulphurous acid existing as bisulphite may, on the other hand, be determined by using standard caustic soda and phenolphthalëin. If commercial bisulphite of soda be diluted with water and a few drops of a solution of methyl orange added, the liquid will assume a red colour in the presence of free sulphurous acid, and the

* *Journ. Soc. Chem. Ind.*, 1884, p. 197.

amount of soda required to discharge the red tint will represent the amount of sulphurous acid in excess of that necessary to form sodium bisulphite. If, however, the liquid be yellow, *normal sulphite* is present, the amount of which may be estimated by titration with standard acid.

SODIUM BORATE, $Na_2B_4O_7 + 10H_2O$, *Borax.* Sodium borate is a salt of tetraboric acid, $H_2B_4O_7$.

Preparation. — It occurs in various districts in India and America in the neighbourhood of dried up lakes. Such natural borax, which is, of course, a crude product, is called *tincal.* The borax is extracted from this raw material by simple lixiviation with hot water, and subsequent crystallisation.

Borax is also made by boiling sodium carbonate solution with boric acid. Borax dissolves in twenty times its weight of water at 15° C., and in half its own weight at 100° C. The liquid has an alkaline reaction. On heating the crystals they swell up and give off their water of crystallisation; at about 560° C. the substance fuses to a glassy mass having the composition $Na_2B_4O_7$.

Borax is used in many industries—*e.g.*, for the soldering of metals, as a starch glaze for linen, and as a mild alkali in the dyeing of some direct cotton colours on cotton and of alkali blues on wool.

Impurities. — Borax may contain as impurities sodium carbonate, sodium chloride, alum, and small quantities of calcium and magnesium salts.

Examination. — The substance should not effervesce on the addition of acids. No precipitate should be formed on the addition of barium chloride or silver nitrate after acidifying the solution with nitric acid.

SODIUM CARBONATE, Na_2CO_3. *Soda Ash, Soda.* Sodium carbonate occurs native combined with 10 molecules of water, and also as *trona* ($Na_2CO_3, 2NaHCO_3, 3H_2O$) in the neighbourhood of the Caspian Sea, in Egypt, and Salt Lake, Utah, U.S.A. The ashes of sea plants, *Algæ*, &c., contain considerable quantities of carbonate of soda.

Preparation. — Sodium carbonate is prepared on the large scale in large quantities by two methods.

(1) *The Le Blanc Process.* - Sodium chloride is treated with sulphuric acid, whereby sodium sulphate is formed :—

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl.$$

The sodium sulphate (salt cake) is then mixed with calcium carbonate and coal, and heated in furnaces, when the following reactions take place :—

$$Na_2SO_4 + 4C = Na_2S + 4CO.$$
$$Na_2S + CaCO_3 = Na_2CO_3 + CaS.$$

The chief constituents of the resulting mass

are sodium carbonate, calcium sulphide, and calcium carbonate. On lixiviating with water sodium carbonate goes into solution, and the calcium compounds remain behind as insoluble substances.

The aqueous extract is evaporated and calcined, the residue forming raw calcined soda. This substance contains sodium hydrate (caustic soda), &c., from which it is purified by recrystallising. The crystals $Na_2CO_310H_2O$, on ignition, form the anhydrous salt.

(2) *The Ammonia Process.*—The carbonate of soda produced by this method contains only small quantities of impurities. A solution of common salt is treated with ammonia gas and carbon dioxide, whereby it is converted into sodium bicarbonate:—

$$NaCl + NH_3 + CO_2 + H_2O = NaHCO_3 + NH_4Cl.$$
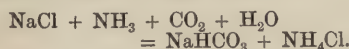
The bicarbonate of soda is then heated and the residue forms the soda ash of commerce :

$$2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O.$$

Properties.—Sodium carbonate is a white solid, which has a caustic taste and an alkaline reaction. 100 parts of water dissolve 16·5 parts at 15° C., 59 parts at 32·5° C., and 45 parts at 100° C. It crystallises from the aqueous solution with 10 molecules of water. Soda ash takes up moisture on exposure to damp air.

Most acids decompose sodium carbonate, carbon dioxide being evolved, and sodium salts of the acid being formed. If carbon dioxide be passed through a solution of sodium carbonate, bicarbonate of soda is produced :—

$$Na_2CO_3 + H_2O + CO_2 = 2NaHCO_3.$$
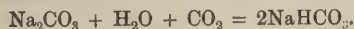
Carbonate of soda possesses similar properties to potassium carbonate. It melts at 814° C., and is slightly volatile at higher temperatures.

Uses.—Sodium carbonate is used for neutralising acids and for fixing ferric and chromic oxide on cotton. It is also employed in wool scouring, in the manufacture of soap, and in the bleaching of cotton goods. It is, next to sulphuric acid, the most important of chemical products.

Commercial sodium carbonate is sold under the name of "soda ash." It comes into the market in various strengths, chiefly 48°, 52° to 56°, and 58°, each degree indicating 1 per cent. sodium oxide, Na_2O.

Soda ash (pure alkali), 58°, contains over 58 per cent. Na_2O, or 98 to 99 per cent. pure sodium carbonate, and is pure enough for almost all technical purposes, especially all dyeing operations. The other brands contain in addition to sodium carbonate, chiefly harmless impurities, like sodium sulphate and chloride ; also some caustic soda, which is

objectionable for some applications, whilst in others its presence is a distinct advantage.

Soda ash dissolves somewhat slowly on account of its forming hard lumps when in contact with water. The tables show the specific gravity of the solution.

SPECIFIC GRAVITIES OF SOLUTIONS OF SODIUM
CARBONATE AT 15° C.

Degrees Twaddell.	Percentage by weight.		Degrees Twaddell.	Percentage by weight.	
	Na_2CO_3.	Na_2O.		Na_2CO_3.	Na_2O.
1	0·47	0·28	16	7·57	4·42
2	0·95	0·56	17	8·04	4·70
3	1·42	0·84	18	8·51	4·97
4	1·90	1·11	19	8·97	5·24
5	2·38	1·39	20	9·43	5·52
6	2·85	1·67	21	9·90	5·79
7	3·33	1·95	22	10·37	6·06
8	3·80	2·22	23	10·83	6·33
9	4·28	2·50	24	11·30	6·61
10	4·76	2·78	25	11·76	6·88
11	5·23	3·06	26	12·23	7·15
12	5·71	3·34	27	12·70	7·42
13	6·17	3·61	28	13·16	7·70
14	6·64	3·88	29	13·63	7·97
15	7·10	4·16	30	14·09	8·24

It is very necessary that the soda ash used in the scouring and milling of textiles previous to dyeing should be as free as possible from iron, as the fibre absorbs the oxide of the metal, which renders it impossible to obtain subsequently any bright shades with mordant colours. The oxide of iron present is also liable to work on to the cloth irregularly, and when such cloth is dyed, dark stains are produced.

Soda ash may be fairly white and yet contain as much iron as another sample with a browner tinge, hence the colour is not to be relied on as proving its absence.

Ammonia soda is free from iron and caustic soda, but generally contains a very slight percentage of bicarbonate. The following is an analysis of ammonia soda ash by Pattinson :—

Sodium carbonate, .	. 98·72	per cent.
,, chloride, .	. 0·54	,,
,, sulphate, .	. 0·20	,,
Magnesium carbonate,	. 0·04	,,
Calcium carbonate, .	. 0·13	,,
Ferric oxide, .	. 0·01	,,
Alumina, .	. 0·01	,,
Silica, .	. 0·09	,,
Moisture, .	. 0·32	,,

Ordinary commercial soda ash (Le Blanc process) should be nearly white and show but few black or red -specs. A soda ash which is white and still contains iron in con-

siderable quantity usually contains sulphites. Sometimes it has a blue shade, probably from sodium manganate. Grey ash denotes a badly manufactured article. It should not contain more than 2 per cent. Na_2O as caustic soda except it be a " caustic soda ash." Sulphide should be absent and traces of sulphate only should be present. The insoluble matter, which consists of calcium carbonate, silica, alumina, and iron, should not exceed 1·5 per cent. The amount of water present is generally 0·5 per cent.

Crystal Carbonate (Gaskell, Deacon & Co.), $Na_2CO_3 + H_2O$, is almost pure carbonate of soda containing, according to the above formula, 14·5 per cent. of water; the commercial product, however, frequently contains about 18 per cent. of water.

This substance is absolutely free from caustic, silica, and alumina, and is superior both in strength and purity to soda crystals, as the following analyses * prove :—

	Soda Crystals.	Crystal Carbonate.
Sodium carbonate, . .	34·22	82·90
,, hydrate, . .	0·10	. .
,, sulphate, . .	2·54	trace
,, chloride, . .	0·27	trace
Water, ...	62·84	17·00
	99·97	99·90
Total soluble impurities on 100 carbonate—*i.e.*, Na_2CO_3,	8·21	0·12
Water on 100 carbonate,	183·64	20·50

Crystal carbonate dissolves much more easily than soda crystals or soda ash, as it does not tend to set in a hard mass at the bottom of the pan like the latter substance.

Five cwts. of crystal carbonate contain as much alkali as 12 cwts. of soda crystals.

A soda ash of extreme purity is made by heating crystal carbonate.

Soda Crystals, $Na_2CO_3 + 10H_2O$.—When chemically pure, soda crystals contain 37·08 per cent. of anhydrous sodium carbonate and 62·92 per cent. of water. They always contain some sodium sulphate, however, this substance being added in small quantity by the manufacturer to produce harder crystals. Owing to the large amount of water in soda crystals the cost of available alkali is more than their equivalent in soda ash when the cost of packages and carriage is taken into account.

Preparation.—Soda ash is dissolved in hot water in iron tanks, the specific gravity of the hot solution being 60° Tw. A little bleaching powder is sometimes added to oxi-

* *Thorpe's Dictionary of Applied Chemistry,* vol. iii.

dise impurities. After settling, the warm liquid is run off into tanks and allowed to crystallise.

The crystals generally contain ½ per cent. of sodium chloride and more or less sodium sulphate.

Analysis of Sodium Carbonate.—Soda ash varies greatly in composition; some qualities consist almost entirely of sodium carbonate, whilst others contain caustic soda (which is desirable for some purposes), as well as sulphides, sulphites, sulphates, iron, calcium, alumina, &c.

In some cases it may only be necessary to determine the total alkali present; in others the caustic soda as well as the carbonate, whilst occasionally, a more complete analysis is required.

Insoluble Matter.—10 grms. of the sample are dissolved in hot water, and filtered into a litre flask, the residue being washed until free from soluble salts. The filter paper and residue are dried, ignited in a crucible and weighed. Then weight of ignited residue × 10 = per cent. of insoluble mineral matter.

Total Alkali.—The filtrate is cooled and made up to 1 litre; 100 c.c. are withdrawn by means of a pipette, and, with methylorange as an indicator, titrated with normal sulphuric acid. Each c.c. of acid required corresponds to 0·031 grm. Na_2O or 0·053 grm. Na_2CO_3.

Caustic Soda.—250 c.c. of the solution (10 grms. per litre) are put into a 500 c.c. flask, an excess of a perfectly neutral solution of barium chloride added, and the flask filled to the mark with distilled water which has been recently boiled and cooled so as to be free from carbonic acid. The flask is well shaken and then allowed to remain at rest until the precipitated barium carbonate has subsided, then 200 c.c. of the clear supernatant liquid (equal to 100 c.c. of original solution) are withdrawn and titrated with $\frac{N}{10}$ sulphuric acid. Either methyl orange or phenolphthaleïn may be used in this case as indicator. Each c.c. of $\frac{N}{10}$ acid corresponds to 0·0031 grm. Na_2O or 0·004 grm. $NaOH$.

If oxalic acid is used in place of sulphuric or nitric acid, the titration may be carried out in the liquid containing the precipitated barium carbonate, the time allowed for settling being thus saved.

Caustic soda may also be determined in a *caustic soda ash* by means of strong alcohol, sodium carbonate being insoluble. For this purpose 2 grms. of the sample are weighed off in a 100 c.c. flask with about 80 c.c. of 96 per cent. alcohol and heated on the waterbath. After cooling, alcohol is added to the mark; the flask is well shaken and allowed to stand for the insoluble carbonate, &c., to subside. 50 c.c. of the clear supernatant

liquid are withdrawn and titrated with $\frac{N}{10}$ acid, as above, using phenolphthaleïn as indicator. Caustic soda may also be separated and estimated by extracting the sample (about 2 to 5 grms.) with 96 per cent. alcohol in a Soxhlet's apparatus. This method is especially to be recommended when it is desired to determine very small quantities of caustic soda in soda ash.

Sodium Carbonate.—From the number of c.c. of normal acid required to neutralise 1 grm. of total alkali, the number of c.c. of the same acid required to neutralise the caustic soda in 1 grm. is deducted, and the difference calculated into sodium carbonate.

Example.—100 c.c. of a solution (10 grms. per litre) of soda ash ($= 1$ grm.) neutralised 16 c.c. of normal sulphuric acid.

1 grm. treated as above for caustic soda $= 20$ c.c. $\frac{N}{10} = 2$ c.c. of normal acid.

$\therefore$ $0.04 \times 2 \times 100 = 8.0$ per cent. NaOH.

$16 - 2 = 14$ c.c. of normal acid corresponding to carbonate.

$\therefore$ $0.053 \times 14 \times 100 = 74.20$ per cent. Na_2CO_3.

Sodium Sulphate is best determined gravimetrically. 200 c.c. of the filtered solution (10 grms. per litre) are acidulated with hydrochloric acid, boiled to expel carbon dioxide, and precipitated with a slight excess of barium chloride, and treated as described under STANDARD SULPHURIC ACID (*v.* ACIDIMETRY).

233 parts of barium sulphate correspond to 142 parts of anhydrous sodium sulphate.

Example.—200 c.c. of the solution ($= 2$ grms.) treated as above yielded 0.1165 grm. barium sulphate.

$\therefore$ $\dfrac{0.1165 \times 100 \times 142}{2 \times 233} = 3.55$ per cent. Na_2SO_4.

Sodium Chloride may be estimated volumetrically by means of silver nitrate, using potassium chromate as an indicator. A decinormal solution of silver nitrate is prepared by dissolving 16.966 grms. of the pure substance in a litre of water. 1 c.c. of this solution $= 0.00355$ grm. chlorine or 0.00585 grm. sodium chloride. Before use this solution should be checked by titrating with it 20 c.c. of a decinormal solution of *pure* sodium chloride, which should require 20 c.c. for the complete precipitation of the chlorine it contains. *Pure sodium chloride* is best prepared by dissolving about 50 grms. of common salt in as little water as possible, filtering and passing hydrochloric acid gas (obtained by quickly heating a mixture of common salt and sulphuric acid in a flask)

into the solution, which is contained in a beaker. It is best to connect the end of the gas delivery tube to a funnel by means of india-rubber tubing and allow the wide portion of the funnel to dip into the liquid, otherwise the end may become blocked with crystals of salt. The sodium chloride is thus completely precipitated, and after decanting the mother-liquor, which contains magnesium chloride, &c., the pure salt is washed with the least possible amount of water, drained, dried in a porcelain dish, and heated over a flame until all hydrochloric acid is volatilised. The salt is pulverised and bottled whilst quite warm. 5.85 grms. of the pure dry sodium chloride are weighed off, dissolved in water and made up to 1 litre.

100 c.c. of the soda ash solution ($= 1$ grm.) are exactly neutralised with $\frac{N}{1}$ nitric acid (having previously determined the total alkali, the exact amount of nitric acid can be added direct) in a porcelain basin, a few drops of a solution of potassium chromate are added, and the $\frac{N}{10}$ silver solution run in from a burette until the liquid acquires a faint orange tint. It is best to deduct from the number of c.c. required 0.1 c.c. for the end reaction, this amount being necessary to cause the change of tint after the chlorine has been recombined.

Example.—100 c.c. of soda ash solution prepared as above and treated as described required 5.1 c.c. $\frac{N}{10}$ $AgNO_3$, after deducting 0.1 c.c. for end reaction $= 5$ c.c.

$\therefore$ $5 \times 0.00585 \times 100 = 2.925$ per cent. NaCl.

The operation depends on the fact that when silver nitrate is added to a neutral mixture of a chloride and a chromate, silver chromate, which is of a crimson colour, is not formed until the whole of the chlorine present in the solution has combined to form silver chloride.

Sodium sulphide is indicated by the evolution of sulphuretted hydrogen when the sample is treated with an excess of hydrochloric acid. Sodium nitroprusside is a more delicate test than this. Filter paper saturated with the reagent is dipped into a solution of the sample; if turned blue-violet a sulphide is present. The amount may be determined by means of a standard solution of ammoniacal silver nitrate. This solution is prepared by dissolving 13.845 grms. of pure silver in pure dilute nitric acid, adding 250 c.c. of $.880$ ammonia, and making up to a litre; 1 c.c. $= 0.005$ grm. sodium sulphide. The operation is performed by adding ammonia to 100 c.c. of the soda ash solution (10 grms. per litre) and heating to boiling. The standard solution of silver is

then run in until no further precipitation of silver sulphide takes place. The exact point can only be ascertained by filtering a few drops of the liquid, and testing the clear filtrate with a drop of the standard silver solution.

Example.—100 c.c. of soda ash solution required 1·5 c.c. ammoniacal silver nitrate. ∴ 1·5 × 0·005 × 100 = 0·75 per cent. Na_2S.

Sodium sulphite, together with sodium sulphide, may be determined by means of a decinormal solution of iodine. Add to 100 c.c. of soda ash solution (10 grms. per litre) an excess of acetic acid and a little starch solution. The iodine solution is dropped in until a blue colour is produced. The amount of iodine required by the sulphide (already determined, if present) is calculated (1 c.c. of $\frac{N}{10}$ iodine = 0·0039 grm. Na_2S), and deducted from the total amount consumed. The difference represents the sodium sulphite present. 1 c.c. of $\frac{N}{10}$ iodine = 0·0063 grm. Na_2SO_3.

Example.—100 c.c. of soda ash solution (10 grms. per litre) treated as above required 1·5 c.c. of ammoniacal silver nitrate for precipitation of the sulphide.

1 c.c. ammoniacal silver nitrate = 0·005 grm. sodium sulphide.

∴ 1·5 c.c. = 0·005 × 1·5 = 0·0075 grm. Na_2S.

Another 100 c.c. soda ash solution required 2·1 c.c. of $\frac{N}{10}$ iodine to produce a blue colour.

1 c.c. $\frac{N}{10}$ iodine = 0·0039 grm. sodium sulphide.

∴ 2·1 c.c. $\frac{N}{10}$ iodine = 0·0039 × 2·1 = 0·00819 grm. sodium sulphide.

0·00819 − 0·00750 = 0·00069 sodium sulphide to be converted into sodium sulphite.

$0·00069 × \frac{63}{39} = 0·0011$ grm. sodium sulphite.

∴ 100 c.c. soda ash contain 0·0011 grm. sodium sulphite.

∴ 0·0011 × 100 = 0·11 per cent. Na_2SO_3.

Except in very crude samples of soda ash, the amount of sulphide and sulphite present is usually very small.

Oxides of Iron and Alumina.—The mixed oxides of iron and aluminium may be estimated by taking about 5 grms. of the sample, dissolving in water, filtering and washing the residue until the washings are neutral to litmus. An excess of hydrochloric acid and a little nitric acid is added to the filtrate, and

the solution, after boiling, precipitated with a *slight* excess of ammonia. The precipitate is washed by decantation, collected on a filter, and thoroughly washed. It is then dried, ignited in a crucible, and weighed.

The amount of iron may be determined in about 5 grms. of the sample by dissolving in water in a flask, adding dilute sulphuric acid free from iron, and boiling to expel carbon dioxide and any sulphuretted hydrogen or sulphur dioxide which may be present. The iron is then reduced to the ferrous state by means of pure zinc, as described under Iron compounds (*q.v.*), and then titrated with $\frac{N}{50}$ potassium permanganate, each c.c. of which corresponds to 0·00112 grm. Fe, or 0·00160 grm. Fe_2O_3.

The amount of ferric oxide obtained is then deducted from the *mixed oxides*, the difference giving the *alumina* present, which, however, will probably include a little silica. The silica, if necessary, may be removed from the solution previous to the precipitation of the mixed oxides, as described under WATER (ANALYSIS OF).

Lime may be estimated in the filtrate from the mixed oxides of iron and alumina by concentrating and adding a slight excess of ammonium oxalate. Since the amount of lime in any case will only be small, the calcium oxalate, after thorough washing, may be taken direct with the filter and ignited in a crucible. When the carbon of the filter has been completely burnt, the crucible is cooled, and a little dilute sulphuric acid cautiously added. After drying on the steam bath, the excess of sulphuric acid is carefully driven off, and the calcium sulphate weighed. 136 parts of $CaSO_4$ = 56 parts CaO.

Water.—Since the value of soda ash and other forms of sodium carbonate is determined by direct analysis, the estimation of water is not of much importance. In the case of a complete analysis, however, it should not be omitted. About 2 grms. of the sample are gently ignited to low redness in a crucible for twenty to thirty minutes. With a carbonated alkali the loss in weight may be directly calculated as water; but if caustic soda is present it will, under ordinary conditions, absorb carbon dioxide with formation of carbonate. A dry soda ash containing caustic soda may be found to be heavier after ignition than before. If the operation is performed in a shallow platinum capsule, the caustic soda present will usually, in the course of an hour or so, become completely converted into carbonate. The conversion into carbonate may be insured by addition of ammonium carbonate. The amount of CO_2 thus absorbed is calculated from the caustic soda present, and added to the loss in weight sustained on heating.

SODIUM CHLORATE, $NaClO_3$. Sodium chlorate is prepared in a similar manner to potassium chlorate, viz., by passing chlorine through a warm solution of caustic soda, filtering off the precipitated sodium chloride, and crystallising the sodium chlorate from the filtrate. It is soluble in its own weight of cold water. This salt is not so expensive as potassium chlorate, and owing to its great solubility it is more suitable for the preparation of aniline black than the potassium salt.

SODIUM CHLORIDE, $NaCl$. *Salt, Rock Salt.* Sodium chloride occurs in extensive beds in Cheshire and elsewhere, and is either mined directly, or, where water has penetrated to the salt, the brine is pumped out. Sometimes a stream of water is turned on to the bed of salt, and the artificial brine is raised and evaporated. Salt is also obtained by the evaporation of sea water. Common salt crystallises from aqueous solutions in cubes. In hot water it is slightly more soluble than in cold; 100 parts of water dissolve at 15° C. 35·9 parts, at 100° C. 39·2 parts of salt. The specific gravity of brine has been determined by Gerlach, who gives the following figures obtained at 15° C. with solution of pure sodium chloride :—

| Per cent. NaCl, .	5	10	15
Specific gravity, .	1·0362	1·0733	1·1114
Per cent. NaCl, .	20	25	26·4 (saturated).
Specific gravity, .	1·1510	1·1923	1·2043

For the preparation of pure sodium chloride see p. 299.

On heating sodium chloride it decrepitates owing to the crystals containing moisture mechanically adhering to them; at 772° it melts, and at a white heat volatilises. Commercial chloride of sodium contains magnesium salts in small quantity, which are deliquescent, hence such salt is always damp. Sodium and calcium sulphate are also present as impurities.

SODIUM HYDROSULPHITE, $NaHSO_2$. *Schuetzenberger's salt.* When iron or zinc is dissolved in sulphurous acid no gas is evolved, but the hydrogen which it is presumed was formed during the first phase of the reaction reduces another molecule of the sulphurous acid, as shown in the following equations :—

$$Zn + H_2SO_3 = ZnSO_3 + H_2.$$
$$H_2 + H_2SO_3 = H_2SO_2 + H_2O.$$

A solution of the sodium salt may be prepared from a concentrated solution of sodium bisulphite by the addition of zinc clippings. The solution should not be allowed to become hot or the reaction will be too violent.

$$Zn + 3NaHSO_3$$
$$= NaHSO_2 + ZnNa_2(SO_3)_2 + H_2O.$$
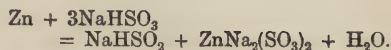
The double sulphite of zinc and sodium being insoluble is precipitated. The solution of sodium hydrosulphite is decanted and kept from contact with air, or it will oxidise to sodium thiosulphate :—

$$2NaHSO_2 = Na_2S_2O_3 + H_2O.$$

The free acid is obtained in solution by the addition of acid to the sodium salt. The solution has a yellow colour, and is easily oxidised. The free acid decomposes on keeping, as also does the sodium salt. It has a stronger reducing action than sulphurous acid, and is a powerful bleaching agent. The sodium salt is used by dyers and printers for reducing indigo, as its action is similar to that of the free acid. Owing to its unstable character only the amount required for immediate use is prepared by the dyer (v. also INDIGO, ANALYSIS OF).

SODIUM HYDROXIDE, $NaOH$. *Caustic soda, Sodium hydrate.*

Preparation.—Sodium hydrate is obtained by boiling a solution of carbonate of soda with lime :

$$Na_2CO_3 + Ca(OH)_2 = CaCO_3 + 2NaOH.$$
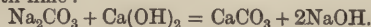
It is also prepared from salt by converting that substance into sodium sulphate and treating the salt cake with calcium carbonate and an excess of carbon in the form of coal. The resulting mass contains a large amount of caustic soda, which is lixiviated and treated with lime to causticise the sodium carbonate, decanted and evaporated.

Sodium hydrate has been prepared commercially by electrolytic processes with more or less success.

Properties.—Caustic soda is a white solid, the commercial article being of various strengths—viz., 48°, 60°, 70°, 74°, 76°, and 77°, each degree representing 1 per cent. of sodium oxide (Na_2O); caustic soda 77° is almost chemically pure sodium hydrate. It is sold in the form of lumps or sticks. It is very hygroscopic and deliquescent, the resulting liquid absorbing carbon dioxide and forming sodium carbonate. Aqueous solutions of sodium hydrate are called caustic soda-lye. Alcohol dissolves caustic soda. Sodium hydrate has very caustic properties; it is a monacid base. It melts at a red heat and volatilises at higher temperatures.

Sodium hydrate is used in large quantities in the manufacture of soap, paper, and dyestuffs; as well as in bleaching, dyeing, and in many other industries.

Analysis.—The strength of a solution of caustic soda may be determined approximately by the hydrometer (see Table). The results, however, are vitiated by the presence of carbonate, sulphate, chloride, &c., of sodium and other salts.

The methods detailed under *sodium carbonate* are used also for caustic soda, the chief difference being that, whereas soda ash, &c., consist essentially of sodium carbonate with (possibly) small quantities of sodium hydrate, commercial caustic soda consists essentially of sodium hydrate, with (possibly) small quantities of sodium carbonate.

Small quantities of carbonate in caustic soda may be conveniently estimated in the following manner :—A weighed amount of the sample is dissolved in about 200 c.c. of cold distilled water (recently boiled and cooled), and a few drops of phenolphthaleïn added. Normal sulphuric acid is slowly and carefully added until the red colour is just discharged. At this point the caustic soda is completely neutralised, and the carbonate converted into bicarbonate. A few drops of methyl orange are now added to the solution, and the addition of normal acid continued until an orange colour appears. The number of c.c. of acid required *after* adding methyl orange, multiplied by 2, represents the amount of sodium carbonate present. Deducting that number from the total amount of acid consumed, the difference represents the sodium hydrate.

Example.—10 grms. of caustic soda were dissolved in 500 c.c. of water. 50 c.c. (= 1 grm.) were taken, diluted with cold (recently boiled) distilled water, phenolphthaleïn added, and titrated with normal acid, as above described. 18 c.c. were required. After adding methyl orange, 0·8 c.c. was required.

1 c.c. of normal acid = 0·040 grm. NaOH.
1 c.c.   ,,   ,, = 0·053 ,, Na_2CO_3.
∴ 0·053 × 1·6 × 100 = 8·48 per cent. Na_2CO_3.

0·040 × 17·2 × 100 = 68·80 per cent. NaOH.

In place of the methyl orange and phenolphthaleïn, Lunge * uses *phenacetolin* for estimating carbonates in the presence of caustic alkalies.

A solution of the indicator of suitable strength is prepared by dissolving 2 grms. in a litre of alcohol. This indicator is of a yellow colour in presence of caustic soda and potash and free mineral acids, but red in presence of carbonates and bicarbonates. A few drops of the indicator are added to the liquid to be tested, and normal acid added until the liquid acquires a rose-red tint. The volume of acid consumed corresponds to the amount of alkali present. The addition of acid is now continued, the liquid becoming a deeper red until it suddenly becomes yellow again. The second volume of acid added corresponds to the amount of sodium carbonate present.

* Journ. Soc. Chem. Ind., 1882, p. 56.

SPECIFIC GRAVITY OF CAUSTIC SODA AT 15°C., PERCENTAGES OF Na_2O AND NaOH (*Schif and Gerlach*).

Per cent. of the Solution.	Specific Gravity for Na_2O.	Specific Gravity for NaOH.
1	1·015	1·012
2	1·020	1·023
3	1·043	1·035
4	1·058	1·046
5	1·074	1·059
6	1·089	1·070
7	1·104	1·081
8	1·119	1·092
9	1·132	1·103
10	1·145	1·115
11	1·160	1·126
12	1·175	1·137
13	1·190	1·148
14	1·203	1·159
15	1·219	1·170
16	1·233	1·181
17	1·245	1·192
18	1·258	1·202
19	1·270	1·213
20	1·285	1·225
21	1·300	1·236
22	1·315	1·247
23	1·329	1·258
24	1·341	1·269
25	1·355	1·279
26	1·369	1·290
27	1·381	1·300
28	1·395	1·310
29	1·410	1·321
30	1·422	1·332
31	1·438	1·343
32	1·450	1·351
33	1·462	1·363
34	1·475	1·374
35	1·488	1·384
36	1·500	1·395
37	1·515	1·405
38	1·530	1·415
39	1·543	1·426
40	1·558	1·437
41	1·570	1·447
42	1·583	1·456
43	1·597	1·468
44	1·610	1·478
45	1·623	1·488
46	1·637	1·499
47	1·650	1·508
48	1·663	1·519
49	1·678	1·529
50	1·690	1·540
51	1·705	1·550
52	1·719	1·560
53	1·730	1·570
54	1·745	1·580
55	1·760	1·591
56	1·770	1·601
57	1·785	1·611
58	1·800	1·622
59	1·815	1·633
60	1·830	1·643

SODIUM HYPOSULPHITE or THIO-SULPHATE, $Na_2S_2O_3 + 5H_2O$. *Antichlor, Hyposulphite of soda.*

Preparation.—A solution of this salt may be prepared by boiling a solution of sodium sulphite with flowers of sulphur :

$$Na_2SO_3 + S = Na_2S_2O_3.$$
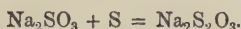
The sodium hyposulphite crystallises from the solution in large colourless prisms containing 5 molecules of water.

The substance is also made from alkali waste.

Properties. — Sodium hyposulphite is a slightly deliquescent salt which easily dissolves in water. On the addition of hydrochloric acid to the aqueous solution sulphur is precipitated and sulphur dioxide is liberated :

$$Na_2S_2O_3 + 2HCl = 2NaCl + SO_2 + S + H_2O.$$

The salt melts on heating and loses its water of crystallisation at 100° C., and on further heating forms sodium sulphate and sodium polysulphide, the latter substance decomposing at higher temperatures, the liberated sulphur taking fire.

It is a strong reducing reagent, and on this account is used in volumetric analysis ; its action on chlorine, bromine, and iodine is shown by the equation—

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6.$$
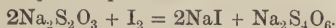
Uses.—Sodium thiosulphate is used sometimes as a mordant for wool. The commercial salt is almost chemically pure. As an antichlor the substance finds application in the bleaching of paper-pulp and textile fibres; the free chlorine being transformed into the non-oxidising compound, sodium chloride, sulphuric acid being also produced.

The thiosulphates evolve sulphuretted hydrogen when treated with zinc and hydrochloric acid.

SODIUM METANTIMONATE *v.* Antimonic Acid.

SODIUM NITRATE, $NaNO_3$. *Chili saltpetre.* Sodium nitrate occurs in large quantities in Peru. It forms rhombohedral crystals, which are hygroscopic and very soluble in water. It melts at 318° C. It is used in the manufacture of saltpetre, nitric acid, nitrites, as a manure, &c.

SODIUM NITRITE, $NaNO_2$. Sodium nitrite is manufactured by reducing sodium nitrate. A large number of methods have been proposed. Le Roy fuses the nitrate with barium sulphide and then extracts the nitrite with water. Lead and iron are also fused with the nitrate, and lixiviated as above. An electrolytic method has been described by A. Dubosc, and E. Divers obtains a pure product by passing nitrous fumes containing slight excess of nitric oxide into concentrated caustic soda.

Sodium nitrite crystals have a faint yellow tinge, and are slightly deliquescent. At the ordinary temperature it is soluble in rather more than its own weight of water. It melts at 213° C. The commercial product contains 93 to 98 per cent. of $NaNO_2$. Sodium nitrite

is used in the manufacture of azo colours and some other dyestuffs, and in the dye-house, for the production of azo colours on the fibre.

Analysis.—Sutton in his seventh edition of *Volumetric Analysis* recommends the method which has been worked out by Kinnicut and Nef, who obtained fair results.

1 grm. of the sample is dissolved in about 300 c.c. of cold water ; to this liquid $\frac{N}{10}$ permanganate is added drop by drop, till it has a permanent red colour ; then 2 or 3 drops of dilute sulphuric acid, and immediately afterwards a known excess of the permanganate. The liquid, which should now be of a dark red colour, is strongly acidified with pure sulphuric acid, heated to boiling, and the excess of permanganate determined by means of freshly prepared $\frac{N}{10}$ oxalic acid.

1 c.c. permanganate = 0·0345 grm. $NaNO_2$, or 0·0425 KNO_2.

SODIUM PARATUNGSTATE *v.* Tungsten.

SODIUM PEROXIDE, Na_2O_2. *Oxygen powder.* This salt has been introduced into commerce as a bleaching agent. It is soluble in water (causing a visible rise of temperature), and possesses a strongly alkaline reaction. When dissolved in dilute mineral acid it yields hydrogen peroxide.

The peroxide as it comes into the market is a yellowish mass, partly powdered. On adding water to a small quantity, any particles of metallic sodium present will ignite. It is very hygroscopic, and if exposed to the air gains 20 per cent. in weight in twenty-four hours. Its powerful oxidising action in the presence of water presents several dangers. Thus, for instance, it may be warmed with aniline or benzene, *in the absence of water*, but on the addition of water the mixture (if particles of metallic sodium be present) at once takes fire.

Peroxide of sodium cannot, by reason of its alkalinity, be employed directly for the bleaching of animal fibres, such as silk or wool. For these fibres it is used as a source of hydrogen or magnesium peroxide. In the latter case a solution of 3 parts of magnesium sulphate (free from chlorine) and 1 part of Na_2O_2 is used ; after treatment with which the goods are lifted, washed with dilute acid and finally with water.

Sodium peroxide is used in analysis for the separation of iron, chromium and manganese, &c.

Analysis.—L. Archbutt (*Analyst*, vol. xx. 1895, p. 3) recommends the following method for the analysis of peroxide of sodium :— About 0·25 grm. of the sample is introduced into the dry tube of a nitrometer flask, and

about 5 c.c. of water (containing a few milligrams of precipitated cobalt sesquioxide in suspension), are placed in the flask itself.

Rapid and complete decomposition of the sodium peroxide results immediately it is brought into contact with water, and the volume of the oxygen evolved is the available oxygen contained in the weight of peroxide taken.

A sample of the commercial substance tested by the above method (except that a drop of cobalt nitrate was used instead of precipitated cobaltic oxide) gave in three experiments 18·54, 18·46, and 18·57 per cent. of available oxygen. The same sample contained 78·66 per cent. of sodium oxide, and 0·49 per cent. of alumina and iron oxide. Hence the calculated composition was:—

Sodium peroxide (Na_2O_2), 90·41 per cent.
Caustic soda (NaOH),　·　8·73　　,,
Alumina and oxide of iron, 0·49　　,,
Undetermined,　　·　·　0·37　　,,

This sample contained a very little carbonate, a trace of chloride, a minute trace of sulphate, and a few particles of unoxidised metallic sodium. No other impurity was detected.

SODIUM PHENOLATE *v.* Phenol.

SODIUM PHOSPHATE, $Na_2HPO_4 + 12H_2O$.

Phosphate of soda is prepared by adding to phosphoric acid a solution of sodium carbonate until the mixture shows an alkaline reaction. On the large scale it is generally made by treating the acid calcium phosphate resulting from the action of sulphuric acid on bone ash with sodium carbonate until no further disengagement of carbon dioxide occurs. The filtrate is concentrated and crystallised.

Properties.—The salt forms large monoclinic crystals which effloresce in the air. The crystals melt at 35° C., lose their water of crystallisation on heating for some time to about 45°, and melt again at 300° C. with formation of sodium pyrophosphate, $Na_4P_2O_7$.

The aqueous solution has a slightly alkaline reaction. The commercial product often contains sodium sulphate, and dissolves in about 25 parts of cold water, and in its own weight of boiling water.

Uses.—Sodium phosphate is used as a substitute for the arsenate in fixing aluminium and iron mordants. It does not, however, always act so well as the arsenate, because aluminium phosphate is not insoluble under certain conditions. Sodium phosphate produces no precipitate in a large excess of aluminium sulphate.

Analysis.—*Chlorine* may be detected by adding nitric acid and silver nitrate to a little of the sample dissolved in water; a white precipitate of silver chloride resulting. The amount of *sulphate* is determined by acidifying an aqueous solution of the salt with nitric acid and treating the precipitated barium sulphate as directed under *acidimetry* (*standard sulphuric acid*).

The percentage of *water* is ascertained by drying a weighed quantity of the salt on the steam bath, then drying inside the bath, and eventually heating to 110° C. until the weight is constant. The loss in weight × 100 ÷ the weight taken = per cent. of water.

The *phosphoric acid* may be estimated by dissolving about 1 grm. of the salt in water, filtering if necessary, and adding to the solution, ammonium chloride (not in excess), ammonia, and magnesium chloride. The beaker containing the solution should be left some time in a warm place, and then allowed to stand for some hours at the ordinary temperature. The supernatant liquid is poured through a filter paper, the white crystalline precipitate of ammonium magnesium phosphate transferred to the filter, and the particles of precipitate still adhering to the sides of the beaker removed by means of a glass rod having a piece of india-rubber tubing slipped over one end, the filtrate being used for washing all on to the filter.

When the whole of the precipitate is on the filter it is thoroughly washed with ammonia water (1 part strong ammonia to 4 parts water), until the filtrate ceases to give more than the faintest opalescence, when a couple of drops are tested with silver nitrate.

The precipitate ($NH_4MgPO_4 + 6H_2O$) is dried in the steam bath, and after detaching from the filter paper transferred to a weighed porcelain crucible, and heated very gently for ten minutes with the lid on. The temperature is then raised until the crucible is red hot. The filter paper, which has been previously folded in a platinum wire, is carefully and completely incinerated (preferably by heating on the crucible lid), and the ash added to the bulk of the precipitate in the crucible. The crucible is then strongly heated over the blowpipe for a quarter of an hour, allowed to cool, and weighed.

The residue consists of magnesium pyrophosphate ($Mg_2P_2O_7$).

The filtrate from the above precipitate is measured, and 0·001 grm. allowed for each 50 c.c., owing to its solvent action on the magnesium ammonium phosphate. This weight is added to the weight of the incinerated precipitate when the calculation is made.

$$\text{Then } \frac{\text{Wt. found} \times P_2O_5 \times 100}{Mg_2P_2O_7 \times \text{Wt. taken}} = \text{per cent. } P_2O_5.$$

SODIUM SILICATE, $Na_2Si_3O_9$. *Silicate of soda, Soluble glass.*

Preparation.—Sodium silicates vary considerably in composition, but the commercial *water-glass* has the composition approximately

represented by the above formula. It is prepared by fusing a mixture of sand and sodium carbonate. The mass is extracted with boiling water. Another method of manufacture consists in boiling caustic soda-lye with powdered quartz under pressure.

Properties.—Sodium silicate is sold in solution or as lumps. The solid dissolves with difficulty in cold, but easily in hot, water. It does not absorb moisture from the air. Dilution of the aqueous liquid tends to cause dissociation into acid and basic salts. Acids precipitate gelatinous silica from the aqueous solution, and even the carbon dioxide from the air slowly decomposes the silicate. The commercial product contains more or less free alkali.

Uses.—Silicate of soda is used for treating curtains, stage decorations, light dresses, &c., in order to make them incombustible. It is also used in the manufacture of soap, partly on account of its detergent action, and partly as "filling." It is employed alone in bleaching, acting as a mild alkali.

In dyeing and calico printing it is used as a fixing agent for "ultramarine blue," &c.; as a substitute for borax in dyeing certain blues and greens; as a "dung substitute," being especially useful for fixing iron and chromium salts. Aluminium salts treated with sodium silicate do not readily attract the colour from the dye-bath, and do not yield such bright shades as when fixed by the arsenate. Any excess of caustic soda in the sodium silicate would form a soluble aluminium salt, and thus remove the mordant from the fibre.

The use of sodium silicate in washing and cleansing wool, cotton, and linen has been investigated, and a comparative examination of the various methods made * with the following results :—

1. For linen cloth, water-glass was found to be far superior to soap, for wool the contrary is the case, and for cotton it is not quite so advantageous.

2. Less work is required when water-glass is used than is the case with soap.

3. Water-glass is much cheaper than soap.

4. The fabric is almost immediately cleansed at boiling heat with water-glass; continued boiling is therefore unnecessary, and would damage the fabric.

5. In a lukewarm solution of water-glass the cleansing proceeds gradually.

6. Linen cloth is damaged by too much rubbing when it is cleansed in a weak soap solution.

7. On linen cloth, the combined use of water-glass and soap produce better results as regards whiteness and solidity; less working is required; increased heat, when required

* *Deutsche Färb. Zeit.*, No. 3, 1885; *Journ. Soc. Dyers and Col.*, 1885, p. 121.

for very dirty and greasy cloths, is harmless.

8. For cotton cloth, the use of water-glass and soap is only advantageous when the temperature is kept at boiling point.

9. For woollen cloths, soap is preferable to water-glass. If it is, however, desired that the cloth should be perfectly cleansed, regardless of loss in weight, the combined use of soap and water-glass at boiling point is to be preferred.

10. On account of its great detergent properties, water-glass is to be recommended for cloths which have ultimately to be bleached.

11. For all sorts of washing, a dilute solution of water-glass is of the greatest importance; the solution should not contain more than 1 per cent.

For washing and elimination of grease from wool water-glass is of no use. The goods are certainly cleansed, but too slowly if a weak solution is used, and, on the other hand, if a strong solution is used, the goods are damaged.

As a brightening or clearing liquor for madder dyes, it is just as bad as soda.

As a dung substitute, it can only be used in a few instances, as most dyes will not stand it and the whites do not come up clear.

In bleaching half-woollen goods, soda is better and cheaper than water-glass. In linen bleaching, soap is superior to water-glass. Soap not only cleanses but imparts to the fabric a nice soft feel after having been submitted to the lime and acid during bleaching.

F. Jean * details an instance of a sophisticated water-glass, the analysis of which was approximately as follows :— Water, 60; Na_2CO_3, 6·5; SiO_2, 21·5; soda combined with silica, 8·5; sulphates and chlorides of iron, alumina, lime, &c., 1·5; and *soda soap*, 2 per cent.

The presence of 2 per cent. of anhydrous soap would cause the solution to be in the form of a jelly, thus giving it the appearance of a concentrated product.

Analysis.—The *water* is determined by gently heating a weighed quantity of the sample (previously dried in the steam bath if liquid) over a very low flame, in a platinum basin, until a constant weight is obtained. The loss = water. If the residue be ignited, the presence of *soap* (if from a liquid sample) may easily be detected by the smell emitted.

Solid alkaline silicates should be very finely ground before dissolving in water.

The *insoluble matter* is estimated by dissolving a portion of the silicate in water and filtering. The filtrate, when cold, may be titrated with normal acid, using methyl orange as indicator. The volume of acid required for neutralisation is calculated to *potash* or *soda*, as the case may be.

* *Chemical News*, vol. xli., p. 251.

The *silica* may be separated from the filtered aqueous solution by adding hydrochloric acid to the liquid contained in a platinum basin, evaporating to dryness, moistening with acid, and after adding water filtering off the precipitated silica (SiO_2). The latter is then washed, dried, ignited, and weighed.

SODIUM STANNATE and STANNITE

v. TIN (STANNATE OF SODA).

SODIUM SULPHATE, Na_2SO_4. *Saltcake,*

Glauber's salt, $Na_2SO_4 + 10H_2O$. Both the anhydrous salt and the hydrated forms occur native in Spain.

Preparation. — Saltcake is obtained by heating common salt with sulphuric acid, hydrochloric acid being also produced. It is used in the manufacture of sodium carbonate by the Le Blanc process, and for glass making. The substance is obtained in a much purer state by lixiviating the saltcake with water and crystallising. *Glauber's salt* separates from the solution as large colourless monoclinic crystals, which, on calcination, form anhydrous sodium sulphate, Na_2SO_4.

Properties.—The calcined salt is hygroscopic and easily soluble in water. A saturated solution, on heating above 33° C., deposits small rhombic crystals of the anhydrous salt. 11 parts of the calcined salt contain the same amount of Na_2SO_4 as 25 parts of the crystallised salt, though otherwise their properties are similar.

Glauber's salt should be crystallised by evaporating solutions of the salt below a temperature of 33° C. On heating the crystals to 33° C. they melt, and on raising the temperature the water of crystallisation is gradually expelled; the anhydrous salt is solid, but melts at a red heat. Glauber's salt contains 44 per cent. Na_2SO_4. The solubility of this substance varies in an abnormal manner, 100 parts of water dissolve at 18° C. 48 parts: at 33° C. 327 parts : and at 100° C. 238 parts of the crystallised salt. Glauber's salt effloresces in the air.

SPECIFIC GRAVITY OF SOLUTIONS OF SODIUM SULPHATE AT 15° C.

Specific Gravity.	Per cent. Na_2SO_4.	Specific Gravity.	Per cent. Na_2SO_4.
1·0091	1	1·0644	7
1·0182	2	1·0737	8
1·0274	3	1·0832	9
1·0365	4	1·0927	10
1·0457	5	1·1025	11
1·0550	6	1·1117	12
		(saturated).	

Uses.—Sulphate of soda in both the forms mentioned above is used by dyers. It is employed in the finishing of cotton goods. It is present in most dyestuffs which are sold as pastes or powders, occurring either as an impurity resulting from the manufacturing process, or having been purposely added either as an adulteration or in order to reduce the colour to a certain standard.

In the case of the direct cotton colours, an addition of this salt to the dye-bath causes the colour to be more rapidly attracted by the fibre.

The acid dyestuffs dye more slowly and evenly when Glauber's salt is added to the dye-bath, as the acidity of the sodium bisulphate which is formed by the decomposition of the sulphuric acid present is not so great as that of the free acid. Again, the addition of sodium sulphate causes the dye to penetrate more deeply into the fibre.

If a basic colour (which is not readily attracted by the fibre in acid solution) be used for shading in an acid bath, the addition of sodium sulphate will neutralise the free acid and enable the fibre to absorb the basic colour.

If a colour which has only feeble dyeing power in an acid bath is to be prevented from dyeing too quickly and unevenly, sulphuric acid is first added, and then sodium sulphate added in small quantities from time to time.

Impurities. — Sodium chloride is always present in greater or less quantity, but for most purposes it is not objectionable. By estimating the amount of chlorine present, the percentage of common salt can be calculated. The anhydrous substance may contain more or less sulphuric acid than is required by the formula Na_2SO_4. The excess of either acid or alkali can be shown by testing with litmus paper, the colour of which is not affected by the normal salt.

Analysis.—Isbert and Venator [*] use the method mentioned below for the rapid and fairly accurate estimation of sodium sulphate in the commercial article.

About 2 grms. of the sample are dissolved in hot water, ammonia and ammonium carbonate are added, and the mixture is filtered; the precipitate is treated with hydrochloric acid on the filter, and the acid liquid thus obtained treated with ammonia and ammonium carbonate. The resulting precipitate is collected and thoroughly washed. A little sulphuric acid is added to the filtrates and washings, which are evaporated in a platinum basin and ignited. The amount of sodium sulphate which existed originally as sodium chloride, and which must be first determined by titration with silver nitrate, is deducted from the weight of the residue. The remainder is the sodium sulphate in the substance weighed off.

Sodium Bisulphate, $NaHSO_4$. *Nitre cake.*

Acid sodium sulphate is obtained by the action of sulphuric acid on sodium sulphate or on common salt or sodium nitrate.

[*] *Zeit. ang. Chem.*, 1889, 66-67.

$$NaCl + H_2SO_4 = NaHSO_4 + HCl.$$
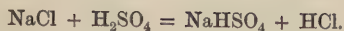
Sodium bisulphate is a white solid which is easily soluble in water. It crystallises with 1 molecule of water.

Uses.—It is used by dyers as a mild acidifying substance, and is preferred in practice to the mixture of sulphuric acid and the normal salt (Na_2SO_4). A probable reason of its superiority for dyeing purposes may be the slowness with which it gives up its acid (it being dissociated in dilute aqueous solution), whereas sulphuric acid does not readily combine with sodium sulphate in dilute solutions. Sodium bisulphate is sometimes sold as *tartar substitute*.

SODIUM SULPHITE, $Na_2SO_3 + 7H_2O.$

Preparation.—The normal salt is manufactured by passing sulphur dioxide into a solution of carbonate of soda until the liquid has an acid reaction. The solution is then boiled, and sodium carbonate added until no further effervescence occurs. The clear liquid is then crystallised.

Properties.—Solutions of the salt deposit monoclinic crystals of the hydrated salt at the ordinary temperature. It contains 50 per cent. of water, and is not hygroscopic. It oxidises on exposure to air forming sodium sulphate. The commercial product is fairly soluble in water, and contains sodium carbonate and sulphate as impurities. It should contain over 22 per cent. of sulphur dioxide, which may be determined by the methods given for this compound.

SODIUM THIOSULPHATE *v.* SODIUM HYPOSULPHITE.

SODIUM THIOSULPHATE (Standard Solution) *v.* CALCIUM CHLORO-HYPOCHLORITE.

SODIUM TUNGSTATE *v.* TUNGSTEN.

SOFTENERS *v.* SIZES.

SOLFERINO. Old name for MAGENTA.

SOLID BLUES *v.* INDULINES.

SOLID GREEN G (D. & H.) *v.* GALLANIL GREEN (D. & H.).

SOLID GREEN O, I, I I (S.C.I.) *v.* BRILLIANT GREEN.

SOLID GREEN O (S.C.I). *Solid green cryst.* (C.) *v.* MALACHITE GREEN.

SOLID GREEN O PASTE (M.), (C.R.) *v.* DARK GREEN.

SOLID VIOLET *v.* GALLOCYANIN.

SOLUBLE BLUE. (All makers.) *Water blue, China blue, Cotton blue, Silk blue, Lyons blue, London blue, Marine blue, Pure blue, Blackley blue, Blue, Acid blue.* Rosaniline derivatives. *Sodium, ammonium, or calcium salts of trisulphonic acids (with di- and tetrasulphonic acids) of triphenyl rosaniline and triphenyl para rosaniline.* 1862. Made by action of concentrated H_2SO_4 on *Spirit blue.* The different marks vary much in purity of shade, corresponding to various degrees of purity of the spirit blue, and of the original magenta. Blue or coppery crystals or powder. Aqueous solution blue. Nearly insoluble in alcohol. Concentrated H_2SO_4, dark, reddish-yellow solution; on dilution, blue solution and precipitate.

Application.—Acid colours. Dye *wool* and *silk* reddish to greenish-blue; also dye tannin-mordanted *cotton.*

SOLUBLE BLUE 8 B, 10 B (Br.S.) *v.* BAVARIAN BLUE D B F.

SOLUBLE BLUE X G (Br.S.) *v.* ALKALI BLUE X G.

SOLUBLE BLUE X L (Br.S.) *v.* BAVARIAN BLUE D B F.

SOLUBLE GLASS *v.* SODIUM SILICATE.

SOLUBLE OIL *v.* TURKEY RED OIL.

SOORANJEE *v.* MADDER.

SORBINE RED (B.). An acid red.

SOUDAN BLACK (P.). An acid black.

SOUPLE SILK *v.* SILK.

SPECIFIC GRAVITY *v.* HYDROMETERS.

SPECIFIC GRAVITY OF FATS *v.* SOAP ANALYSIS.

SPIRIT BLUE *v* GENTIANA BLUE 6 B.

SPIRIT EOSIN *v.* EOSIN S AND PRIMROSE.

SPIRIT YELLOW G (K.) (C.R.) *v.* ANILINE YELLOW.

SPIRIT YELLOW R (K.). An azo dye.

Orthotoluidine — Orthotoluidine.

1877. Orange yellow powder almost insoluble in water. Soluble in alcohol with a yellow colour. In concentrated H_2SO_4 brown solution; on dilution, red, then red ppt.

Application.—Used in colouring butter, margarine, &c.

SPIRITS OF HARTSHORN *v.* AMMONIA.

SPIRITS OF SALT *v.* HYDROCHLORIC ACID.

SPIRITS OF WINE *v.* ALCOHOL.

STANDARD SOLUTIONS *v.* ACIDIMETRY (Sulphuric Acid, Hydrochloric Acid, Caustic Soda); *v.* SODIUM (Silver Nitrate); *v.* SODIUM CARBONATE, ANALYSIS (Silver Nitrate, Sodium Chloride); *v.* GLYCERIN (Potassium Bichromate); *v.* CALCIUM CHLORO-HYPOCHLORITE (Sodium Arsenite, Sodium Thiosulphate); *v.* IRON (Potassium Permanganate).

STANLEY RED (Cl. Co.) *v.* CLAYTON CLOTH RED.

STANNIC AND STANNOUS SALTS *v.* TIN.

STARCH *v.* THICKENERS.

STARCHES. The two kinds of starch chiefly used as thickeners are maize or Indian corn starch and wheat starch.

Preparation.—Maize is softened by steeping in running water at 135° F. for three days. It is then ground and sieved systematically with a stream of water. The milky liquid is allowed to settle and the sediment washed repeatedly. It is then treated with dilute caustic soda, washed as before and collected in moulds, broken up and eventually dried.

Properties.—Starch, $(C_6H_{10}O_5)n$, is a white uncrystallisable solid, having a granular

texture. The grains when subjected to microscopic examination exhibit a series of concentric rings, the nucleus of which varies in position in different starches, as do also the size and shape of the grains.

Starch is almost insoluble in cold water; on heating, however, the starch cells burst and a viscous liquid termed starch paste is formed. This substance forms a jelly on cooling.

Iodine gives a blue coloration with starch; the colour disappears on heating the solution, but returns on cooling.

On boiling starch with dilute acids, dextrin ($C_6H_{10}O_5$) and eventually dextrose ($C_6H_{12}O_6$) are produced. Diastase at 60° C. converts starch solution into dextrin and maltose ($C_{12}H_{22}O_{11}$). Heat has a very similar action on the dry substance.

Starch can be rendered soluble in water by heating under pressure with steam. Delory states that the product seems well adapted for sizing and finishing yarns and fabrics, and serves well as a thickening material.

Very often gum tragacanth is mixed with starch paste used in calico printing, as the mixture keeps better than starch paste alone.

Starches should always be examined for *grit*, by making a thin paste with cold water on a porcelain slab, and feeling for any traces of grit with a spatula. Freedom from grit in all the materials used in calico printing cannot be too much insisted upon.
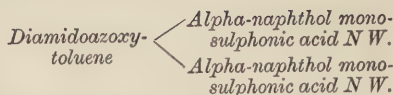
A portion of the sample should be boiled and made into a paste, which should be compared with a standard sample as regards *colour, consistency*, &c.

Water and *ash* should be estimated, and a *microscopical examination* should be made.

Estimation of Starch.—P. L. Hibbard [*] gives the following method for a quick estimation of starch :—1 grm. is put into a flask with 50 c.c. of water and 2 c.c. of malt extract. It is at once heated to boiling with frequent shaking. After one minute the liquid is cooled to 55° C., 3 c.c. of malt extract added, and the solution slowly heated for fifteen minutes until boiling, again cooled and tested with iodine solution. If the starch has all disappeared, the mixture is cooled, made up to a definite bulk and filtered through fine muslin. An aliquot part of the filtrate (containing 0·2 to 0·3 grm. of starch) is boiled with 5 c.c. of 30 per cent. hydrochloric acid and sufficient water to make the bulk up to about 60 c.c. for half an hour on a sand-bath. The solution is cooled, neutralised with dilute caustic soda, and the dextrose determined gravimetrically with Fehling's solution.

ST. DENIS RED (P.) (Ber.). An azoxyazo dye.

[*] *Journ. Amer. Chem. Soc.*, 1895, vol. xvii., pp. 64-68.

Diamidoazoxy-toluene ⟨ Alpha-naphthol mono-sulphonic acid N W.
Alpha-naphthol mono-sulphonic acid N W.

1887. Red powder. Aqueous solution, red; slightly soluble in alcohol. Concentrated H_2SO_4, red solution; on dilution, red ppt.

Application.—A direct cotton dye applied by a special process.

STEARIC ACID, $C_{18}H_{36}O_2 = C_{17}H_{35}$ (CO.OH). Stearic acid closely resembles palmitic acid. It is a white substance which melts at 69° C., and can be distilled under diminished pressure without being decomposed. It is a monobasic acid and its salts are called *stearates*. These salts have similar properties to the palmitates (*v.* SOAPS).

Stearin or *Tristearin*, ($C_{18}H_{35}O_2)_3C_3H_5$, the glycerin ether of stearic acid, melts at 72° C., and yields the acid by saponification. Stearin occurs in all solid animal fats, and is best prepared from mutton fat or shea butter. Stearic acid is one of the chief constituents of ordinary soap.

STEROSINE GREY (H.). Brownish-black paste, smelling of acetin. Black solution in water; alcoholic solution, reddish-blue. Concentrated H_2SO_4, brown solution; on dilution, bluish-brown.

Application.—Dyes in neutral bath on *wool* or mixed goods, producing bluish-greys.

STICK LAC *v.* LAC DYE.

STILBENE ORANGE 4 R & STILBENE YELLOW G, 6 G (Cl. Co.). Direct cotton colours.

STILBENE RED, G (Ber.). Obsolete azo dye. Dyes cotton direct.

STYROGALLOL. An oxyketone dye. *Dioxyanthracoumarin.* 1886. A mordant dye. No longer used.

SUDAN G (Ber.) (Fi.). *Carminnaphte ?* (D. & H.), *Cerasine orange G* (L.). An azo compound.

Aniline — Resorcinol.

1875. Brown powder, almost insoluble in water; soluble in alcohol or ether with a light yellow colour. Concentrated H_2SO_4, brownish-yellow solution; on dilution, light brown ppt.

Application. — Used in colouring lakes, spirit varnishes, &c.

SUDAN I. (Ber.) (Fi.). *Carminnaphte* (D. & H.). An azo compound.

Aniline — Beta-naphthol.

1883. Brick-red powder, insoluble in water; soluble in alcohol with an orange-red colour. Concentrated H_2SO_4, magenta-red solution; on dilution, orange-red ppt.

Application.—As SUDAN G.

SUDAN II. (Ber.). *Red B* (B.) (Fi.). An azo compound.

Xylidine — Beta-naphthol.

1883. Brownish-red powder, insoluble in water; in alcohol, yellowish-red solution. Concentrated H_2SO_4, magenta-red solution; on dilution, pale yellow ppt.

Application.—As SUDAN G.

SUDAN III. (Ber.) (Fi.). *Cerasine red* (C.), *Red C* (B.). An azo compound.

Amidoazobenzol — *Beta-naphthol.*

1879. Brown powder, insoluble in water. Alcoholic solution, red. Concentrated H_2SO_4, green solution; on dilution, blue solution, then red ppt.

Application.—As SUDAN G.

SUDAN R (Ber.). A similar product.

SUDAN BROWN (Ber.) (Fi.). *Pigment brown* (B.). An azo compound.

Alpha-naphthylamine — *Alpha-naphthol.*

1878. Brown powder, insoluble in water. Alcoholic solution, brown. Concentrated H_2SO_4, blue solution; on dilution, brown ppt.

Application.—v. SUDAN G.

SUDAN RED v. MAGDALA RED.

SUGAR OF LEAD v. LEAD ACETATE.

SUINT v. WOOL; also WOOL FAT.

SULPHAMIN BROWN A (D.). *Naphthaline brown α* (P.). An azo dye. 1894. Brown powder, soluble in water. In concentrated H_2SO_4 green solution, on dilution, brown solution.

Application. — A mordant dye. Dyes chrome-mordanted *wool* brown.

SULPHAMIN BROWN B (D.). *Naphthaline brown β* (P.). An azo dye. 1894. Brown powder. Aqueous solution yellowish-brown. Concentrated H_2SO_4, violet solution becoming yellowish-brown on dilution.

Application.—A mordant dye, giving chocolate-brown shades on chrome-mordanted *wool.*

SULPHANILIC ACIDS, $C_6H_4.NH_2.SO_3H$, are the sulphonic acids of aniline. The para compound is the one most commonly met with, and is prepared by heating aniline sulphate to 180° to 210° C. for several hours.

Properties.—It crystallises from water in large colourless, rhombic plates, containing 1 molecule H_2O. The free acid is sparingly soluble in cold water, but its Na & K salts are easily soluble.

Uses.—Sulphanilic acid is employed in colour making (v. ORANGE I., II., III., &c.) and as a developer (v. AZO DYES *produced on cotton.*

SULPHANIL YELLOW (B. K.). An azo dye.

Benzidine $\Big\langle$ *Sulphanilic acid.*
Sulphanilic acid.

1884. Brownish-yellow powder. Aqueous solution greenish-yellow.

Application.—A direct cotton colour. Dyes unmordanted *cotton* greenish-yellow.

SULPHATED OIL v. TURKEY RED OIL.

SULPHIDE COLOURS. This class of colouring matters is rapidly becoming one of the most important in the dyeing of cotton and other vegetable fibres. The general reaction for their preparation consists in the fusion of aromatic diamines and other organic bodies with sodium sulphide and sulphur or with thiosulphates. They are applied in an alkaline bath, with or without addition of sodium sulphide, and are usually fixed by a subsequent treatment with some oxidising agent.

The group includes brown, black, and navy-blue dyes, which are amongst the fastest colours known.

Greens.

Katigen Green.	Katigen Olive.

Blues.

Immedial Blue C.	Kryogen v. Blue
Immedial Sky Blue.	G, R.
	Melanogen Blue B.

Blacks.

Anthraquinone Black.	Immedial Black.
Carbide Black.	Katigen Black.
Clayton Fast Black.	Saint Denis Black.
Cross Dye Black.	Sulphanil Black.
Eclipse Black.	Thiogene Black.
Fast Black B & B S.	Vidal Black.

Browns.

Cachou de Laval.	Kryogen Brown.
Eclipse Brown.	Sulphaniline Brown.
Immedial Brown.	Thiocatechin.
Katigen Black Brown N.	

SULPHIN (B.) v. PRIMULINE.

SULPHINDIGOTIC ACID v. INDIGO (SULPHONIC ACID).

SULPHONAZURIN (By.). An azo dye.

Benzidine sulphon $\Big\langle$ *Phenyl beta-naphthylamine.*
disulphonic acid $\Big\langle$ *Phenyl beta-naphthylamine.*

1883. Dark greyish-blue powder. Aqueous solution, blue. Concentrated H_2SO_4, violet solution; on dilution, black-violet precipitate.

Application.—A direct cotton colour. Dyes unmordanted *cotton* or *wool* blue.

SULPHOCYANIC ACID v. CHROMIUM SULPHOCYANIDE.

SULPHOCYANIN G (By.). Dark blue powder. Aqueous and alcoholic solution, bright blue. Concentrated H_2SO_4, reddish-blue solution; on dilution, greenish-blue to bright blue.

Application.—A direct cotton dye. Specially suitable for wool dyeing. Gives dark navy blue shades with mordant.

SULPHOCYANIN G R EXTRA, 3 R, 5 R EXTRA are similar colours.

SULPHOLEIC ACID *v.* OLEIC ACID.

SULPHOPURPURIC ACID *v.* INDIGO (SULPHONIC ACID).

SULPHUR, $S = 32$. This substance occurs in nature in the free state in volcanic districts, particularly in Sicily.

Preparation.—The crude material, mixed with earthy impurities, is heated in earthenware pots; the molten sulphur runs out into receivers and thence into cold water. The rough sulphur is then distilled, the condenser being in the form of a large brickwork chamber. The sulphur condenses in the form of fine crystals (flowers of sulphur) on the walls. The molten sulphur which collects on the floor of the chamber is run into moulds, and constitutes *roll sulphur.*

Properties.—Ordinary sulphur crystallises in octahedra. Two other allotropic modifications exist, differing from the ordinary form in crystalline form and solubility in carbon bisulphide.

Sulphur has a lemon-yellow colour, and is very brittle. It is a bad conductor of heat and electricity. On heating, it melts at 115° C., forming a thin liquid; at a higher temperature it becomes darker in colour, and at 250° C. it is so viscid that it is almost solid; on heating further it becomes more mobile, and at 440° C. it boils. It is soluble in carbon bisulphide. Sulphur is a very active chemical element. It burns in the air when ignited, forming sulphur dioxide. It combines with carbon at a red heat, forming carbon disulphide (CS_2). If a current of hydrogen be passed through molten sulphur, hydrogen sulphide (SH_2) is produced. Sulphur is used as a bleaching agent by burning it (stoving), and in the preparation of sulphuric acid.

SULPHUR DIOXIDE, SO_2. When sulphur burns in air a pungent smelling gas, having the above composition, is produced.

Preparation.—Sulphur dioxide is prepared by heating copper turnings with strong sulphuric acid.

$$Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2.$$

On the large scale, sulphur, or the ores of sulphur, are roasted with free access of air.

Properties.—Sulphur dioxide is a colourless gas, having the pungent odour characteristic of burning sulphur. At a pressure of 2 atmospheres, or when cooled to −15° C., it is condensed to a colourless liquid. The liquid substance is a commercial article.

Sulphur dioxide is very soluble in water, 51 volumes of the gas being absorbed at 10° C. The solution has the characteristic smell of the gas, and is considered as a solution of sulphurous acid (H_2SO_3). Boiling expels the gas gradually. The liquid has a strong acid reaction, and, on exposure to air, oxidises slowly to sulphuric acid.

Sulphur dioxide does not support combustion, and neither plants nor animals can exist in an atmosphere containing even relatively small quantities of the gas.

When a mixture of the dried gases, oxygen and sulphur dioxide are passed over gently-heated platinum black, sulphur trioxide is formed :—

$$2SO_2 + O_2 = 2SO_3.$$
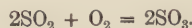
Sulphur dioxide, both in the gaseous form and in solution, is a strong reducing agent. Potassium bichromate is reduced by this substance to chromium sulphate. Sulphuretted hydrogen, however, reduces sulphur dioxide to sulphur.

$$SO_2 + 2H_2S = 2H_2O + 3S.$$
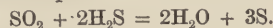
Uses.—Sulphur dioxide is used as a bleaching agent for wool, silk, straw, sponges, &c. It is owing to its reducing action that sulphur dioxide possesses bleaching properties. Many organic colouring matters are decolorised by sulphur dioxide, nascent hydrogen being the real cause of the reaction.

$$SO_2 + 2H_2O = H_2SO_4 + H_2.$$

It is used as an *antichlor* for removing the last traces of chlorine from bleached material.

$$SO_2 + Cl_2 + 2H_2O = H_2SO_4 + 2HCl.$$
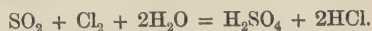
Sulphur dioxide is also employed as a disinfectant.

SULPHUROUS ACID, H_2SO_3. This acid is unknown in the free state; aqueous solutions of sulphur dioxide probably contain this compound. A hydrate, $SO_2 + 15H_2O$, can be obtained as crystals from the concentrated solution at 0° C. Sulphurous acid is a dibasic acid, and forms neutral salts or *sulphites* like Na_2SO_3, and acid salts or *bisulphites* resembling $NaHSO_3$.

Metasulphites of sodium and potassium exist. They have the composition $Na_2S_2O_5$ and $K_2S_2O_5$ formed thus :—

$$2NaHSO_3 - H_2O = Na_2S_2O_5.$$

SULPHURIC ACID. *Oil of Vitriol,*
$H_2SO_4 = SO_2{<}^{OH}_{OH}.$

Preparation.—This acid is produced by the oxidation of sulphur dioxide by means of nitric acid. Sulphur dioxide, obtained by burning sulphur or iron pyrites, is introduced into leaden chambers together with air, steam, and nitrous gases.

$$SO_2 + NO_2 + H_2O = H_2SO_4 + NO.$$
$$NO + O = NO_2.$$

The oxides of nitrogen are alternately reduced by the sulphur dioxide and oxidised by the air. Although the above equations give a general idea of the reactions which take place, the chemistry of the various changes actually occurring in the chambers has not been fully explained.

The sulphuric acid which collects on the floors of the chambers has a specific gravity of 1·6, and is known as *chamber acid*. By concentration in leaden pans to 1·7 the so-called brown oil of vitriol (B.O.V.) is obtained. On further concentrating the product in glass or platinum vessels, the commercial concentrated sulphuric acid (O.V. or D.O.V.,—*i.e.*, double O.V.) is produced. This acid still contains up to 7 per cent. of water. If this product be distilled, water and dilute acid constitute the first part ($\frac{1}{3}$) of the distillate, the latter part of the distillate passing over at 330° C. and constituting almost pure sulphuric acid. It has a specific gravity of 1·84 at 15° C. It still contains about 1·5 per cent. of water. If the acid be cooled to a low temperature, *anhydrous* acid solidifies in the form of crystals, which, on separating and melting, have the specific gravity 1·8372 at 15° C., hence the monohydrate has about the same density as a 95 per cent. acid, and a 98 per cent. acid has the highest specific gravity. The strength of commercial sulphuric acid may be brought up to that of the monohydrate (H_2SO_4) by the addition of fuming sulphuric acid. The acid commences to become solid below 0° C., and melts again at 10·5° C.

Properties.—Sulphuric acid is very hygroscopic and readily abstracts the elements of water from many substances; thus alcohol, on heating with the acid, forms ethylene (C_2H_4); oxalic acid is resolved into carbon monoxide and carbon dioxide; sugar, starch, and vegetable fibres are completely decomposed and charred (carbonised).

On mixing sulphuric acid with water a great development of heat is occasioned, the resulting mixture, after cooling, occupying less volume than the original constituents of the mixture. Great care should always be observed in mixing sulphuric acid with water; *the acid should be poured into the water very slowly in a thin stream*, the mixture being *stirred* meanwhile, and the water used should be *cold*. Water must *on no account* be poured into sulphuric acid. Sulphuric acid which has been diluted with an equal weight of water does not give off much heat on further diluting.

Vessels *filled* with the concentrated acid will overflow if exposed to the air for some time, owing to the absorption of water.

Sulphuric acid is dibasic, and forms neutral salts resembling K_2SO_4 (sulphates), and acid salts like $KHSO_4$ (bisulphates or acid sulphates).

Sulphuric acid is a very strong acid, forming salts of all metals and displacing most other acids from combination.

Oil of vitriol dissolves almost all metals except lead and platinum; it has very little effect on iron, although dilute sulphuric acid quickly dissolves it.

$$H_2SO_4 + Fe = FeSO_4 + H_2.$$

Impurities. — Commercial sulphuric acid contains, besides more or less water, other impurities—viz., arsenic, lead, iron, selenium, sulphur dioxide, and nitrous gases. It is, however, generally sufficiently pure for the use of the dyer. A small quantity of organic matter (straw, &c.) will cause otherwise pure acid to become quite brown.

Lead sulphate and oxides of nitrogen may be got rid of by distillation with a small quantity of ammonium sulphate.

Uses.—Sulphuric acid is manufactured on a very large scale, and is used in most chemical industries, in the production of dyestuffs and various mordants, &c.

It is employed in bleaching, mordanting, and dyeing for the carbonisation of woollen material, &c.

Fuming or *Nordhausen sulphuric acid* is sulphuric acid containing varying quantities of sulphur trioxide (sulphuric anhydride), SO_3.

It is prepared by heating ferrous sulphate, $FeSO_4 . 7H_2O$, which at a moderate heat loses its water of crystallisation. The partially dehydrated salt, on more strongly heating, is decomposed thus:—

$$2FeSO_4 = Fe_2O_3 + SO_2 + SO_3.$$
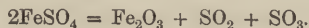
The water which still remains attached to the salt then combines with part of the SO_3 to form sulphuric acid, and this unites with another molecule of SO_3 forming ($H_2SO_4 + SO_3$). This acid fumes on exposure to air.

The number of pounds of H_2SO_4 per gallon is found by multiplying the number in the fourth column (kilo. per litre) by 10 (p. 312).

The exact temperature at which the density is taken must be noted and, if necessary, corrections made, otherwise the results will be incorrect. A difference of 2° C. in the temperature may, if neglected, cause an error of 3 per cent. of sulphuric acid calculated from the tables.

Analysis of Sulphuric Acid—Total Acid by Titration.—25 c.c. of the sample are accurately weighed in a beaker and poured into a litre flask half full of water; after washing out the beaker, the flask is cooled and the solution filled up to the mark. 25 c.c. are withdrawn and titrated with $\frac{N}{1}$ caustic soda and methyl orange. 1 c.c. = 0·049 grm. H_2SO_4. Lunge observes that if the acid to be tested contains an appreciable quantity of nitrous acid, methyl orange cannot be employed as

PERCENTAGE AND SPECIFIC GRAVITY OF SULPHURIC ACID AT 15°C. (*Otto*).

Per cent. by weight, H_2SO_4.	Specific Gravity.	Per cent. by weight, SO_3.	Per cent. by weight, H_2SO_4.	Specific Gravity.	Per cent. by weight, SO_3.	Per cent. by weight, H_2SO.	Specific Gravity.	Per cent. by weight, SO_3.
1	1·0064	0·816	11	1·0756	8·98	21	1 1516	17·14
2	1·0130	1·630	12	1·0830	9·79	22	1·1590	17·95
3	1·0190	2·445	13	1·0910	10·61	23	1·1670	18·77
4	1·0256	3·260	14	1·0980	11·42	24	1·1740	19·58
5	1·0320	4·080	15	1·1060	12·24	25	1·1820	20·40
6	1·0390	4·890	16	1·1136	13·06	26	1·1900	21·22
7	1·0464	5·710	17	1·1210	13·87	27	1·1980	22·03
8	1·0536	6·530	18	1·1290	14·69	28	1·2066	22·85
9	1·0610	7·340	19	1·1360	15·51	29	1·2150	23·67
10	1·0680	8·160	20	1·1440	16·32	30	1·2230	24·49

SPECIFIC GRAVITY AT 60° F. (15⅚° C.) (*Lunge and Isler*).

Degrees Twaddell.	100 parts by weight contain SO_3.	H_2SO_4.	Kilo. per litre H_2SO_4.	Degrees Twaddell.	100 parts by weight contain SO_3.	H_2SO_4.	Kilo. per litre H_2SO_4.	Degrees Twaddell.	100 parts by weight contain SO_3.	H_2SO_4.	Kilo. per litre H_2SO_4.
40	22·30	27·32	0·328	86	43·36	53·11	0·759	132	60·11	73·64	1·222
41	22·82	27·95	0·337	87	43·75	53·59	0·769	133	60·46	74·07	1·233
42	23·33	28·58	0·346	88	44·14	54·07	0·779	134	60·82	74·51	1·244
43	23·84	29·21	0·355	89	44·53	54·55	0·789	135	61·20	74·97	1·256
44	24·36	29·84	0·364	90	44·92	55·03	0·798	136	61·57	75·42	1·267
45	24·88	30·48	0·373	91	45·31	55·50	0·808	137	61·93	75·86	1·278
46	25·39	31·11	0·382	92	45·69	55·97	0·817	138	62·29	76·30	1·289
47	25·88	31·70	0·391	93	46·07	56·43	0·827	139	62·64	76·73	1·301
48	26·35	32·28	0·400	94	46·45	56·90	0·837	140	63·00	77·17	1·312
49	26·83	32·86	0·409	95	46·83	57·37	0·846	141	63·35	77·60	1·323
50	27·29	33·43	0·418	96	47·21	57·83	0·856	142	63·70	78·04	1·334
51	27·76	34·00	0·426	97	47·57	58·28	0·866	143	64·07	78·48	1·346
52	28·22	34·57	0·435	98	47·95	58·74	0·876	144	64·43	78·92	1·357
53	28·69	35·14	0·444	99	48·34	59·22	0·886	145	64·78	79·36	1·369
54	29·15	35·71	0·454	100	48·73	59·70	0·896	146	65·14	79·80	1·381
55	29·62	36·29	0·462	101	49·12	60·18	0·906	147	65·50	80·24	1·392
56	30·10	36·87	0·472	102	49·51	60·65	0·916	148	65·86	80·68	1·404
57	30·57	37·45	0·481	103	49·89	61·12	0·926	149	66·22	81·12	1·416
58	31·04	38·03	0·490	104	50·28	61·59	0·936	150	66·58	81·56	1·427
59	31·52	38·61	0·500	105	50·66	62·06	0·946	151	66·94	82·00	1·439
60	31·99	39·19	0·510	106	51·04	62·53	0·957	152	67·30	82·44	1·451
61	32·46	39·77	0·519	107	51·43	63·00	0·967	153	67·65	82·88	1·463
62	32·94	40·35	0·529	108	51·78	63·43	0·977	154	68·02	83·32	1·475
63	33·41	40·93	0·538	109	52·12	63·85	0·987	155	68·49	83·90	1·489
64	33·88	41·50	0·548	110	52·46	64·26	0·996	156	68·98	84·50	1·504
65	34·35	42·08	0·557	111	52·79	64·67	1·006	157	69·47	85·10	1·519
66	34·80	42·66	0·567	112	53·12	65·08	1·015	158	69·96	85·70	1·534
67	35·25	43·20	0·577	113	53·46	65·49	1·025	159	70·45	86·30	1·549
68	35·71	43·74	0·586	114	53·80	65·90	1·035	160	70·94	86·90	1·564
69	36·14	44·28	0·596	115	54·13	66·30	1·044	161	71·50	87·60	1·581
70	36·58	44·82	0·605	116	54·46	66·71	1·054	162	72·08	88·30	1·598
71	37·02	45·35	0·614	117	54·80	67·13	1·064	163	72·69	89·05	1·621
72	37·45	45·88	0·624	118	55·18	67·59	1·075	164	73·51	90·05	1·639
73	37·89	46·41	0·633	119	55·55	68·05	1·085	165	74·29	91·00	1·661
74	38·32	46·94	0·643	120	55·93	68·51	1·096	166	75·19	92·10	1·685
75	38·75	47·47	0·653	121	56·30	68·97	1·107	167	76·27	93·43	1·713
76	39·18	48·00	0·662	122	56·68	69·43	1·118	167·6	77·23	94·60	1·739
77	39·62	48·53	0·672	123	57·05	69·89	1·128	167·8	77·55	95·00	1·748
78	40·05	49·06	0·682	124	57·40	70·32	1·139	168	78·04	95·60	1·759
79	40·48	49·59	0·692	125	57·75	70·74	1·150	168·2	79·19	97·00	1·786
80	40·91	50·11	0·702	126	58·09	71·16	1·160	168·3	79·76	97·70	1·799
81	41·33	50·63	0·711	127	58·43	71·57	1·170	168·2	80·16	98·20	1·808
82	41·76	51·15	0·721	128	58·77	71·99	1·181	168	80·98	99·20	1·825
83	42·17	51·66	0·730	129	59·10	72·40	1·192	167·8	81·39	99·70	1·834
84	42·57	52·15	0·740	130	59·45	72·87	1·202	167·7	81·59	99·95	1·838
85	42·96	52·63	0·750	131	59·78	73·23	1·212				

indicator, unless the nitrous acid is previously oxidised by potassium permanganate.

The strength of the acid may also be ascertained by running the dilute solution from a burette into a solution of pure carbonate of soda. If 1·082 grm. of sodium carbonate is taken, the number of c.c. of acid required to neutralise it contains exactly 1 grm. of H_2SO_4.

Example.—25 c.c. of sulphuric acid weighing 46 grms. were diluted to a litre.

1·082 Na_2CO_3 neutralised 22·5 c.c. acid.

∴ 22·5 c.c. acid contain 1 grm. H_2SO_4.

∴ 1000 c.c. contain $\dfrac{1000}{22\cdot5} = 44\cdot44$ grms. H_2SO_4.

∴ $\dfrac{44\cdot44 \times 100}{46} = 96\cdot60$ per cent. H_2SO_4.

Sodium sulphate is sometimes present (*v.* below, *Sulphate of Lead*).

Sulphate of lead is indicated by the formation of a white precipitate on dilution with water. It may be estimated by taking 25 c.c. of the sample and adding 25 c.c. of water and 50 c.c. of alcohol. The liquid is filtered and the precipitate washed *thoroughly* with alcohol. The lead sulphate is dried, ignited in a porcelain crucible and weighed. This determination, however, is not often necessary; it usually suffices to ignite about 10 grms. of the acid in a crucible and weigh the residue. The amount obtained, which, as a rule, is very small, of course includes *sodium sulphate*, if present.

Iron is detected by boiling the diluted acid with a drop of nitric acid. If, after cooling, a solution of potassium sulphocyanide causes a red coloration, iron is present. Iron may be determined by igniting 10 to 20 grms. and treating the residue as mentioned under *Water Analysis*.

The direct estimation of iron by reduction with zinc and subsequent titration with potassium permanganate cannot be recommended, since arsenic, if present, would seriously interfere with the reaction.

Nitrous Acid is determined by titrating the diluted solution with $\frac{N}{2}$ potassium permanganate.

Nitrogen Acids.—Nitrogen compounds in sulphuric acid are especially mischievous in acid used for dissolving indigo, since a portion of the colouring matter is thereby destroyed, and the resulting extract is not so bright. They may be detected by carefully pouring a solution of ferrous sulphate into a test tube containing the acid, the formation of a brownish-purple ring where the two liquids meet indicating the presence of oxides of nitrogen. A more delicate method is the following :—25 to 50 c.c. of the acid are diluted with half the volume of water, and a drop of a 1 per cent. alcoholic solution of diphenylamine added. The liquid, on stirring with a glass rod, becomes coloured blue in the presence of nitrogen acids. The depth of the coloration is in proportion to the amount present. On standing the colour gradually disappears.

According to Lunge, this test fails, however, in the presence of selenium (which can be recognised by adding to the acid a strong solution of ferrous sulphate, when a brownish-red precipitate will make its appearance, which cannot be confounded with the colour produced by the test for NO mentioned above). If selenium be present the nitrogen acids are detected by the addition of brucine sulphate solution to the diluted acid, a red colour demonstrating their presence.

Arsenic, if present in considerable quantities (which is often the case with acid made from pyrites), is readily detected by diluting about 25 c.c. with 150 c.c. of water, and passing a current of sulphuretted hydrogen through the liquid. A yellow precipitate indicates arsenic, which may further be confirmed by treating the precipitate with a strong solution of ammonium carbonate, in which reagent arsenious sulphide is soluble.

If a yellow precipitate from a given weight of acid (about 50 grms.) be collected on a weighed filter paper, washed thoroughly, dried at 100° C., and weighed, the amount of arsenic present may be ascertained.

246 parts of the precipitate $As_2S_3 = 198$ parts of As_2O_3. Small quantities of arsenic are best detected and estimated by Marsh's test (*v.* TEXTILE FABRICS (ANALYSIS OF).

SUMAC.—The plants which produce this tannin are various species of *Rhus*, nat. order *Anacardiaceæ*. They are found in most countries which have a temperate climate, and were used as a source of tannic acid as early as the time of Pliny. The chief commercial varieties are the following * :—

Sicilian,	.	*Rhus coriaria.*
Italian,	.	*R. coriaria.*
Spanish,	.	Several varieties.
Tyrolese,	.	*R. cotinus.* (The wood of this tree constitutes *Young Fustic.*)
French,	.	Varieties of *coriaria.*
Algerian,	.	*R. pentaphyllum* (used by the Arabs in preparing morocco leather.
North American,		*R. glabra, R. canadensis, R. typhina.*
Swiss,	.	*Arbutus uva ursi.*

* "*Culture of Sumac,*" U.S. Dept. of Agriculture. M'Murtie. 1889.

Some varieties of *Rhus* yield a resinous juice, which is used in the preparation of (Japanese) lacquer. Other species are poisonous—*e.g.*, "Poison ivy" (*R. toxicodendron*) and "Swamp dog-wood" (*R. venenata*).

The most esteemed varieties are Sicilian and Italian sumac, then follow Spanish, Portuguese, and North American, while French, Swiss, and Hungarian (Tyrolese) are less valuable. Algerian is not much exported.

The most important variety, *R. coriaria*, is a tall shrub, 8 to 15 feet high. The leaves of the plant, which constitute the commercial article, are 1 to 2 inches long, covered with short hairs, and green or greyish-green in colour. They are either torn to shreds or ground to a fine powder before use. Extracts of sumac are also much used. Sumac contains from 15 to 20 per cent. tannic acid and a small amount of yellow and red colouring matters, which are fixed along with the tannin, and render cotton prepared with sumac unsuitable for the production of some light shades. Several excellent brands of bleached sumac extract are, however, now sold.

SUMAC TANNIC ACID *v.* TANNIC ACID.

SUNFLOWER SEEDS yield a glucoside, *helianthic acid*, which, when hydrolysed, produces a blue or violet dye.

SUN YELLOW (G.) (L.) (By.) (Ber.) *v.* CURCUMIN S.

SUPERARGOL *v.* POTASSIUM ACID TARTRATE.

SYLVINE *v.* POTASSIUM CARBONATE.

T

TABORA BLACK (Ber.). Black powder, aqueous solution reddish - blue. Slightly soluble in alcohol. Concentrated H_2SO_4, bright blue solution; on dilution, becomes reddish-violet.

Application.—A direct cotton dye. Used direct or developed with toluylene diamine or naphthylamine ether.

TAGARA SILK *v.* SILK (WILD).

TALC *v.* MAGNESIA.

TALLOW is the oleaginous substance obtained by melting beef and mutton fat. Inferior qualities extracted from bones, the solid parts of fish and vegetable fats are also used in the manufacture of soap.

Properties.—Pure tallow is white in colour, but the commercial tallows are generally yellow. The chief constituents are olein and stearin, with a smaller amount of palmitin. The melting point of a good sample is 110° F. (43·5 C.). Tallow is often adulterated with starch, China clay, whiting, bone grease, cotton-seed stearin, and the distilled fatty acids from wool grease.

Analysis.—*Insoluble matter* may be detected by dissolving the fat in ether, and filtering off the residue.
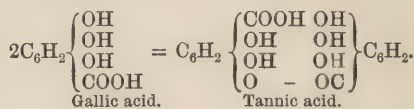
Unsaponifiable matter, mineral and fatty acid, may be determined, as in OILS (LUBRICATING). For constants of tallow *v.* SOAP.

The solidifying point of the fatty acids or titer test is carried out as in SOAP ANALYSIS. For the manufacture of candles it should not be below 44° C.

TANNIC ACID. *Gallotannic acid, Sumac tannic acid, Digallic acid*—

$$C_{14}H_{10}O_9\ 2H_2O.$$
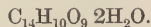
This body exists naturally in gall nuts, sumac, and other tannin matters, and may also be produced synthetically by the condensation of gallic acid :—

$$2C_6H_2\left\{\begin{matrix}OH\\OH\\OH\\COOH\end{matrix}\right. = C_6H_2\left\{\begin{matrix}COOH & OH\\OH & OH\\OH & OH\\O & - & OC\end{matrix}\right\}C_6H_2.$$

Gallic acid.   Tannic acid.

It is most readily obtained from gall nuts.

Commercial Tannic Acid.—Three varieties of this product are distinguished, these being obtained respectively by extraction with ether, with alcohol, or with water; the purity of the products varying with the method of extraction.

Chinese and Japanese galls are the best source of tannic acid, since they contain less colouring matter than oak galls. The purest commercial tannic acid is prepared as follows[*]: —The crushed galls are stirred with sufficient water to form a concentrated solution, the temperature employed being 40° to 60° C. When the liquor is sufficiently concentrated, it is run off and allowed to cool and settle for twelve hours. It is then run through a filter into a closed drum, in which it is agitated with about one-quarter its volume of ether (0·750 sp. gr.) for several hours. The emulsive liquid thus produced is run into closed tanks, and allowed to remain at rest for from eight to ten days, during which time it gradually separates into two layers. The upper ethereal layer, which contains most of the impurities, is drawn off and the ether recovered by distillation, the lower layer being also separately distilled for recovery of the ether, until it acquires a syrupy consistency. After cooling, this is spread in thin layers on a plate heated by steam, when it almost immediately swells up to a bulky pale-coloured mass.

The so-called "tannic acid crystals" are prepared by forcing the syrupy liquid obtained on evaporating off the ether, through a plate perforated with fine holes, on to a hot cylinder,

[*] Trimble, *The Tannins*, vol. i., p. 82.

where the tannic acid solidifies in slender needles which have the appearance of crystals.

Alcohol Tannin is prepared by extracting the galls with dilute (50 per cent.) alcohol, and after allowing any solid matter to settle out, evaporating the clear solution to dryness. The resinous mass is then ground to powder.

Water Tannin is prepared by extracting with water instead of alcohol, and evaporating to dryness in vacuum pans. It is a somewhat less pure product.

Preparation of Pure Tannic Acid.—The purest commercial tannic acid contains small amounts of fat, resin, colouring matter, gallic acid, and glucose. These may be removed by dissolving in ether, to which just sufficient water has been added to effect solution, shaking well and allowing to settle. Three layers are formed, the lowest of which contains nearly pure tannic acid.

Another process, devised by Trimble, and which gives a very pure product, is conducted as follows:—10 grms. of commercially pure tannic acid are dissolved in 200 c.c. water, then a 10 per cent. solution of lead acetate is added, drop by drop, with continued stirring, until the character of the precipitate changes from the original granular yellow form, becoming white and amorphous. The solution is then filtered, and agitated successively with three portions, each of 75 c.c. of pure ether. The mixed ethereal extracts are distilled to dryness, when a light, colourless, porous residue of tannic acid remains. This contains traces of gallic acid, which may be removed by dissolving in a small quantity of distilled water, agitating with ether to dissolve the gallic acid, and evaporating the aqueous solution to dryness in a partial vacuum.

Properties of Tannic Acid.—Tannic acid possesses a strongly astringent taste, but is odourless. On exposure to light it becomes brown, even in the absence of air. It is soluble in six parts of cold water, and very soluble in hot water, the solution having an acid reaction. It also dissolves easily in glycerin, but with difficulty in alcohol. It is insoluble in ether, chloroform, carbon disulphide, or benzene.
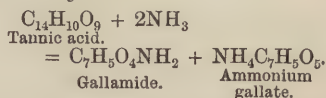
Tannic acid is precipitated from its aqueous solution on addition of sulphuric, hydrochloric, arsenic, or boric acid, but is not precipitated by nitric acid. On heating with dilute mineral acid it undergoes hydrolysis, with production of gallic acid—

$$C_{14}H_{10}O_9 + H_2O = 2C_7H_6O_5.$$
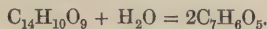
Commercial tannic acid under the same conditions yields glucose and ellagic acid in addition to gallic acid.

Caustic potash or soda also brings about a similar decomposition of tannic acid. Ammonia behaves differently, forming, in the absence of oxygen, a mixture of *gallamide* and *ammonium gallate*—

$$C_{14}H_{10}O_9 + 2NH_3$$

Tannic acid.

$$= C_7H_5O_4NH_2 + NH_4C_7H_5O_5.$$

Gallamide. Ammonium gallate.

Many neutral salts, such as sodium chloride, calcium chloride, &c., also precipitate free tannic acid from its aqueous solution. On the other hand, it decomposes carbonates with evolution of carbon dioxide and production of tannates. It also displaces sulphuric or hydrochloric acid from those salts, with the metal of which it forms an insoluble tannate—*e.g.*, *iron, aluminium, tin, antimony, copper, manganese,* &c. *Ferrous salts* give a white precipitate, which gradually becomes blue or black by absorption of oxygen. *Ferric salts* produce a blue coloration or black precipitate, according to the concentration of the solution. If very dilute, however, or in presence of tartaric acid, the colour is greenish. Ferric tannate is soluble in dilute (mineral) acids, but is reprecipitated by sodium acetate. A mixture of ferrous and ferric tannates, with or without the addition of Prussian blue, and slightly thickened with gum arabic, constitutes the better kinds of writing ink; a little carbolic acid or other antiseptic being added. Many lead tannates have been prepared and described, the particular salt obtained depending upon the conditions of formation.

Tannic acid precipitates solutions of *glue, gelatine, starch,* or *albumen,* and combines with animal skins to form leather. It also precipitates most alkaloids and other organic bases. When heated to a temperature of 120° to 140° C., tannic acid darkens in colour without undergoing decomposition, but at 160° it is decomposed with production of *pyro-* and *metagallic acids* ($C_6H_3(OH)_3$), carbon dioxide, and water. At higher temperatures no pyrogallic acid is formed. On heating with arsenic acid *ellagic acid* is produced.

Solutions of tannic acid have a reducing action, precipitating cuprous oxide from Fehling's solution. By the cautious oxidation of an aqueous or alcoholic solution of tannic acid, a yellow colouring matter—galloflavin—is formed. Ammonium molybdate gives a reddish-yellow precipitate with tannic acid, which substance also produces a brilliant red colour with a solution of iodine in potassium iodide made slightly alkaline with ammonia. A dilute ammoniacal solution of potassium ferricyanide (red prussiate of potash) also gives a red colour, which is destroyed by excess of the reagent.

Tannic acid is not a glucoside, but the tannins from which it is produced are glucosides, and glucose is an invariable constituent of commercial tannic acid.

Tannic acid is used in pharmacy, in dyeing, and in printing, and in the preparation of inks and dyestuffs, pyrogallol, gallic acid, &c.

SPECIFIC GRAVITY OF SOLUTIONS OF TANNIC ACID AT 15° C. (*Trammer*).

Specific Gravity.	Per cent. Tannic Acid.	Specific Gravity.	Per cent. Tannic Acid.
1·0040	1·0	1·0124	3·1
1·0044	1·1	1·0128	3·2
1·0048	1·2	1·0132	3·3
1·0052	1·3	1·0136	3·4
1·0056	1·4	1·0140	3·5
1·0060	1·5	1·0144	3·6
1·0064	1·6	1·0148	3·7
1·0068	1·7	1·0152	3·8
1·0072	1·8	1·0156	3·9
1·0076	1·9	1·0160	4·0
1·0080	2·0	1·0164	4·1
1·0084	2·1	1·0168	4·2
1·0088	2·2	1·0172	4·3
1·0092	2·3	1·0176	4·4
1·0096	2·4	1·0180	4·5
1·0100	2·5	1·0184	4·6
1·0104	2·6	1·0188	4·7
1·0108	2·7	1·0192	4·8
1·0112	2·8	1·0196	4·9
1·0116	2·9	1·0200	5·0
1·0120	3·0		

Analysis v. TANNIN MATTERS.

TANNIN BROWN B (C). Greenish-black powder, aqueous solution brown. Red solution in alcohol. Concentrated H_2SO_4, reddish-brown solution; on dilution, bluish-red, then brown.

Application.—A basic colour.

TANNIN HELIOTROPE (C.) *v.* GIROFLÉE (D. & H.).

TANNIN INDIGO (D. & H.). A basic dye.

TANNIN MATTERS. Tannic acid is found in a large number of vegetable products, those in which this or other similar bodies exist in large amount being classified as *tannin matters*.

Tannin matters are obtained from various portions of plants, one of the most important sources being *gall nuts*, which are excrescences produced upon various species of oaks by the puncture of an insect. Certain barks, leaves, unripe fruit, and woods also constitute tannin matters. These all contain similar, but not identical, essential constituents, which are generally spoken of as *tannins*, tannic acid itself being found in largest quantity in gall nuts, but also in many other tannin matters, some of which, however, do not contain tannic acid, but other closely allied substances, such, *e.g.*, as *ellagitannic acid*.

The tannic acid obtained from various sources is called *gallo*-tannic acid, *sumac*-tannic acid, &c., according to its origin.

Tannin matters possess the following characteristics :—They have an astringent, bitter taste, and a feeble acid reaction ; they produce a blue or green coloration or precipitate with iron salts, and combine with animal membrane to form an insoluble and non-putrescible substance termed leather. They also produce an insoluble precipitate in an aqueous solution of albumen or gelatine.

Preparation of Tannin Matters.—The tannin matters are employed in dyeing either in the form of powder or as extracts. Myrabolans and valonia are very difficult to grind and are usually treated in powerful crushing and grinding machines. Sumac is most easily reduced to powder by grinding in a mill consisting of a revolving wooden or cast-iron bed in which run two heavy rollers armed with projecting studs.

Tannin Extracts.—These are prepared by extracting the tannin matters with hot water, either in open vessels or, more usually, under slight pressure, and concentrating the extract thus obtained in vacuum pans. Previous to the extraction, barks or woods are reduced to small chips, and galls, myrabolans, &c., are broken or ground.

The most usual strength of the commercial extracts is about 51° Tw., the syrupy liquid of this strength keeping without much deterioration for a long time in closed receptacles, whereas when much more dilute they rapidly ferment.

Decolorising Tannin Extracts.—On account of the objectionable tints imparted to cotton by the yellow, red, and brown colouring matters present in various tannin matters and their extracts, some cheap method of destroying or removing these colours without injury to the tannin has long been desired, and several brands of "colourless" or "decolorised" myrabolans and sumac extracts are now in the market.

The decolorisation may be brought about in various ways, of which the following appear the most generally adopted :—

1. The extract is thoroughly agitated with bullock's blood, and the precipitated impurities removed by straining.

2. Fractional precipitation of the extract with some metallic salt, the following having been proposed :—Sodium bisulphite, ammonium sulphate, magnesium sulphate, strontium hydrate, bismuth nitrate, lead acetate, or zinc acetate. The two latter, particularly the lead salt, are most commonly used.

A process which is said to give satisfactory results is carried out as follows :—The extract is diluted to about 1·025 specific gravity (5° Tw.), and 250 to 500 grms. acetate of lead are added to every 1000 litres of liquor. The mixture is agitated for one to three hours at 60° to 70° C., exactly neutralised with borax or sodium phosphate and filtered, most of the impurities remaining upon the filter.

Chemistry of Tannin Matters.

The chemical nature of many of the tannins is still involved in much obscurity, and it is uncertain whether many of them are distinct substances or are identical with one or other of the better recognised tannins.

All tannins are amorphous, astringent bodies, and have feeble acid reactions. They produce blue or green colorations or precipitates with iron salts, and precipitate albumen and gelatine from aqueous solution. Most of them have the property of transforming animal skins into leather.

Various classifications of the tannins have been proposed, the oldest being the distinction of "iron-bluing" and "iron-greening" tannins. It has, however, been recently found that the same tannin may produce both blue and green precipitates with iron salts, according to the acidity or alkalinity of the solution.

Another classification, due to Wagner, divides tannin into "pathological," which are formed by the puncture of an insect, and "physiological" tannin, which occurs naturally in vegetable tissue.

The first group includes all the varieties of galls, while all other tannins would be classed as *physiological*, although some have been proved to be chemically identical with gallo-tannic acid. For use in tanning leather they are conveniently classified into those which do, and those which do not produce upon leather a brown deposit, termed "bloom." This property is found to exist in those which normally produce a blue colour with iron salts.

When heated to 160° C. the tannins are decomposed, and may again be divided into two classes, according to the products which they yield, this classification closely approximating to the last. The "iron-bluing" tannins which produce "bloom" on leather yield metagallic acid and *pyrogallol*, while "iron-greening" or "non-blooming" tannins produce metagallic acid and *catechol*.

Analysis of Tannins.—A great variety of processes have been devised for estimating tannic acid in the substances known as "*tannins*." The majority of the published methods have had the valuation of tannins for tanning leather mainly in view, but it does not necessarily follow that these methods are equally serviceable for valuing tannins for use in dyeing.

Procter's modification of Löwenthal's process [*] is very generally adopted in testing the materials used both for tanning and for dyeing purposes.

Owing to the impossibility of obtaining absolutely pure tannic acid for the purpose

of standardising the potassium permanganate solution, which is used to oxidise the tannin substances, and to the fact that the commercial tannins contain more or less gallic acid, which is also acted on by permanganate, it is not possible to estimate the exact amount of tannin. By strictly adhering to one method of manipulation, however, in the manner in which the analysis is carried out, good comparative results between similar kinds of material can be obtained.

The operation is performed in two stages, a solution of indigo-sulphonic acid being used as an indicator. In the first place the total oxidisable matters are determined, and in another portion of the solution the tannic acid is precipitated by gelatin, and the oxidisable matters other than tannin are estimated in the filtered solution. The difference between the two titrations expresses the amount of tannic acid in terms of standard permanganate.

In precipitating the tannic acid by gelatin, Procter saturates the solution with salt. Hunt [*] has shown that a considerable amount of gallic acid is likewise precipitated under these conditions, and recommends that the liquid be only one-quarter saturated with salt. Unfortunately some of the tannic acid is thereby left in solution. Rawson has compared the results obtained by various modifications of the above processes with the results obtained by dyeing-trials on the same samples. The following method, which differs but little from Procter's or Hunt's processes,[†] was adopted. The following solutions are required :—

Standard Permanganate.—An $\frac{N}{50}$ solution of potassium permanganate is prepared by dissolving 0·632 grm. of the pure recrystallised salt in a litre of water. The solution is standardised by pure ferrous ammonium sulphate, or pure oxalic acid (*v.* Iron, Ferrous Salts). 1 c.c. $\frac{N}{50}$ KMnO$_4$ = 0·00126 grm. of crystallised oxalic acid.

Indigo Solution.—1 grm. of pure indigotin dissolved in 50 c.c. of pure concentrated sulphuric acid, and diluted with water to 1 litre.

Gelatin Solution.—20 grms. of fine gelatin (Nelson's) are soaked in water for about three hours, and then dissolved on the water-bath in a litre of water. The liquid is saturated with salt and filtered. The solution should be used while fresh.

Sulphuric Acid and Salt.—A 5 per cent. solution of sulphuric acid is saturated with purified sodium chloride.

[*] *Journ. Soc. Chem. Ind.*, 1885, p. 263.
[†] For fuller particulars concerning these methods, see Procter's *Leather Industries Laboratory Book*, Allen's *Commercial Organic Analysis*, vol. iii., and Sutton's *Volumetric Analysis*.

[*] *Journ. Soc. Chem. Ind.*, 1884, p. 82; and 1886, p. 79.

Titration for Total Oxidisable Matters.— About 2 grms. of the sample (more or less according to the amount of tannin probably present) are boiled with 500 c.c. of distilled water in a flask for half an hour. The liquid is allowed to stand a few minutes and then is quickly cooled, 5 c.c. of a 10 per cent. solution of acetic acid added, and the whole diluted to 500 c.c. After shaking well it is poured into a tall glass cylinder and the insoluble matter allowed to subside. [The decoction should not be filtered, since filter paper absorbs tannic acid to a considerable extent, and the amount abstracted from solution depends on the rate of filtration.] When the insoluble matters have sufficiently subsided, which may take an hour or so, 10 c.c. of the clear solution are carefully withdrawn and mixed with 500 c.c. of water in a large porcelain basin, 25 c.c. of the indigo solution are added, and $\frac{N}{50}$ KMnO$_4$ run in from a burette in continuous drops during constant and vigorous stirring until the liquid becomes of a light green colour. The permanganate is now added more slowly until the green coloration has given place to yellow, when a faint but unmistakable pink rim round the edge of the basin may be observed. 25 c.c. of the indigo solution with 500 c.c. of water are titrated alone, and the number of c.c. of permanganate required is deducted from the previous result. The difference expresses the total amount of oxidisable matters in 10 c.c. of the decoction.

Titration of Oxidisable Matters other than Tannin.— 50 c.c. of the clear decoction are introduced into a stoppered bottle of about 200 c.c. capacity and 25 c.c. of the gelatin and salt solution added; after mixing, 25 c.c. of the acid salt solution are added, and the whole well shaken. The liquid is thus practically half saturated with salt. After standing for half an hour it is filtered and 40 c.c. of the filtrate (= 20 c.c. of the original solution) mixed with 500 c.c. of water and 25 c.c. of the indigo solution, and titrated with permanganate as before. If there is a difficulty in obtaining a clear filtrate, a little kaolin or barium sulphate may be shaken up with the liquid before filtering. In the case of myrabolans and sumac, however, the filtrate is usually clear without any addition of this kind.

Example.—2 grms. of myrabolans were extracted and made up to 500 c.c., as above described. 10 c.c. titrated direct with 25 c.c. of the indigo solution required 29·5 c.c. of $\frac{N}{50}$ KMnO$_4$. 25 c.c. of indigo alone required 16·5 c.c. of $\frac{N}{50}$ KMnO$_4$.

Total oxidisable matters in 10 c.c., therefore, equal to 29·5 − 16·5 = 13 c.c. of $\frac{N}{50}$ KMnO$_4$. 40 c.c. of the filtrate from

gelatin precipitate (= 20 c.c. of the original solution) required with 25 c.c. of indigo solution 23·2 c.c. of $\frac{N}{50}$ KMnO$_4$.

Oxidisable matters other than tannin in 20 c.c., therefore, equal to

23·3 − 17* = 6·2 c.c. of $\frac{N}{50}$ KMnO$_4$.
= 3·1 ,,   ,,   in 10 c.c.
∴ 13 − 3·1 = 9·9 c.c. of $\frac{N}{50}$ KMnO$_4$ consumed by the tannic acid in 10 c.c. of the infusion. The percentage of tannin is commonly expressed in terms of oxalic acid.

$$\frac{0·00126 \times 9·9 \times 50 \times 100}{2} = 31·18 \text{ per cent.}$$

of tannic acid expressed as oxalic acid.

According to Neubauer and Oser, 0·063 of oxalic acid corresponds to 0·04159 of gallotannic acid (gall-nut tannin) or 0·06235 of quercitannic acid (oak-bark tannin). The percentage of tannic acid expressed in terms of oxalic acid multiplied by 0·666 gives, therefore, the percentage of gall-nut tannin; and multiplied by 0·99, the percentage of oak-bark tannin.

Commercial tannic acid and *extracts* of sumac, myrabolans, &c., are examined in the same way as natural tannins, the boiling with water being omitted. About 1 grm. of tannic acid, or 2 to 5 grms. of "extracts," dissolved in 500 c.c. of water will give solutions of convenient strength. In place of gelatin, specially prepared *hide powder* is often used to precipitate the tannin matters. 50 c.c. of the decoction of tannin are treated with 3 grms. of hide powder for a period of eighteen hours (shaking occasionally) and then filtered. 10 or 20 c.c. of the filtrate are titrated as described above. Concordant results are obtained, but, on account of gallic acid and oxidisable substances other than tannin being abstracted from the solution, the method cannot be recommended for dyeing purposes.

For similar reasons Procter's gravimetric process† is not a good method for the valuation of dyers' tannin substances.

Hide powder is carried out as follows :—50 c.c. of a clear infusion of the tannin (containing about 1 per cent. of tannin) are evaporated to dryness at 100° C. and weighed. About 100 c.c. of the same solution are filtered by upward filtration through a layer of hide powder contained in a bottle from which the bottom has been removed, and a glass tube in the form of a syphon, fixed in the bottle neck by means of a caout-

* 0·5 c.c. of KMnO$_4$ is here allowed for the action of oxidisable matters introduced by the gelatin. This should be determined by means of a blank experiment.

† *Journ. Soc. Chem. Ind.*, 1887, p. 94.

chouc stopper. The bottle and its charge of hide powder are placed in a beaker, into which the liquid to be tested is poured, and when the powder is saturated the solution is syphoned over. The beaker is kept filled with the tannin liquor. The first 30 c.c. of the filtrate, which has syphoned over, is rejected. 50 c.c. of the filtrate is evaporated as before and weighed. The difference between the two results represents the amount of tannin in 50 c.c.

Gerland determines tannin by means of a solution of tartar emetic prepared by dissolving 2·611 grms. of the crystals dried at 100° C. in 1 litre of water. A few grains of thymol will preserve the liquid for a considerable time. 1 c.c. = 0·005 grm. tannin. 50 c.c. of the tannin solution are taken for titration, 2 grms. of ammonium chloride added and titrated with the solution of tartar emetic until no further turbidity is produced. The titration is finished when a drop of the antimony solution ceases to cause a turbidity with a drop of the tannin solution placed on a piece of black glass.

Becker * has devised the following process : —5 grms. of methyl-violet are dissolved in 1 litre of hot water, and, when cold, filtered. 10 grms. of the purest tannin, well dried, are dissolved in water and made up to 1 litre. 10 grms. of the sample of tannic acid (or 20 to 40 grms. of sumac, &c.) are also dissolved and made up to 1 litre, the moisture having been previously determined.

50 c.c. of the methyl-violet solution are run from a burette into a beaker, and, with 450 c.c. of water, heated to 50° C. The pure tannin solution is then slowly dropped in from a second burette, stirring well until all the colouring matter is thrown down. This is ascertained to be the case when a small portion gives a colourless filtrate. If the filtrate is still coloured it is poured back to the bulk and more tannin solution added. Good filter paper must be used, otherwise the liquid passes through turbid. When it has thus been found how much pure tannin is needed to decolorise 50 c.c. of the coloured liquid, the solution of tannin under examination is treated in the same way, and its *relative value* is calculated from the figures obtained.

Procter considers " that with such varied and little understood bodies as the tannins, the mode of analysis must be chosen in relation to the use to which the materials are to be put. If the object is to precipitate antimony, naturally Gerland's tartar emetic process is more likely to give good results than a gelatin process. If ink making or dyeing black is the requirement, Handke's process with ferric acetate, or a colorimetric method, would suggest itself. If fixing aniline colours is required, an aniline colour,

* *Chemical News,* vol. li., p. 229.

such as methyl-green, may be used as a precipitant. In all these methods we are not really determining the *quantity* of a given ingredient present, but the *activity* in a special direction of a mixture of various compounds. It is therefore most essential that the chemist should *specify* not only his results but *how his results are obtained*. In the case of most tannin materials the *sampling, grinding, and extraction are as important* and as likely, if unsystematically carried out, to lead to discrepancies *as any other part of the process.*"

Examination of Tannins by Dye-trials.—Whichever method of analysis is used for estimating tannic acid, the results should always be confirmed by making experimental dye-tests. The exact mode of procedure may vary according to the kind of tannin under examination and the uses to which it is to be put, but the following can be recommended for general purposes :—2 grms. of each sample (myrabolans, sumac, &c.) are boiled for fifteen minutes with half a litre of water. The decoctions (with the insoluble portion) are made up exactly to 500 c.c., and poured into beakers, which are then introduced into a steam bath. 10 grms. of common salt are added to each beaker, and when the temperature is uniform (about 95°) 10 grms. of cotton yarn (previously thoroughly wetted) are introduced. The yarn is worked on glass rods dipping beneath the surface of the liquid, and the solutions allowed gradually to cool. After standing, at least three hours, the yarn is taken out and the excess of liquid removed by pressure (not washed), and each hank introduced into separate beakers containing 200 c.c. of basic ferric sulphate (nitrate of iron), of specific gravity 1·01 (2° Tw.). After fifteen or twenty minutes the yarn is taken out, washed, dried, and the depth of shade compared. *It is most important that* in each series of tests *the conditions* as to temperature, time, amount of water used, &c., *should be exactly the same for each sample.*

TANNIN ORANGE R PASTE (C.). A basic azo dye.

Amidobenzyl dimethylamine — Beta-naphthol.

Reddish-brown paste, soluble in water with an orange colour, and in alcohol with a brownish-yellow colour. Concentrated H_2SO_4, bluish-red solution ; on dilution, yellowish-orange.

Application.—A basic colour. Dyes tannin-mordanted *cotton* bright reddish-orange.

TARTAR v. POTASSIUM BITARTRATE.

TARTAR EMETIC v. ANTIMONY (POTASSIUM ANTIMONY TARTRATE).

TARTARIC ACID, $C_4H_6O_6 = \begin{cases} CO(OH) \\ CH(OH) \\ CH(OH) \\ CO(OH) \end{cases}$
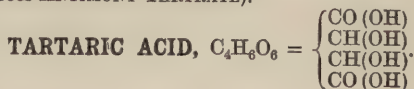
(*Ordinary tartaric acid, Dextro tartaric acid*). The juice of the grape deposits *tartar* (acid potassium tartrate) during the fermentation of wine.

Preparation. — Tartaric acid is obtained from the crude tartar. The latter substance is first purified by crystallisation, and then boiled with water and powdered chalk ; the products of this reaction are neutral potassium tartrate (which is readily soluble) and neutral calcium tartrate, which, being insoluble, separates out as a white powder. The filtered solution of neutral potassium tartrate is treated with calcium chloride solution, whereby all the tartaric acid is precipitated as the neutral calcium salt. The calcium tartrate is decomposed by means of dilute sulphuric acid, the calcium sulphate is filtered off and the filtrate evaporated until the tartaric acid crystallises.

Properties. — Tartaric acid forms large transparent prisms of strong acid taste, which melt at 170° C., and are decomposed at higher temperatures without distilling ; it is easily soluble in water but less so in alcohol. Tartaric acid is a strong dibasic acid ; its salts are known as *tartrates*.

Uses. —Tartaric acid is frequently employed in dyeing and printing, both in the free state and in the form of the acid potassium salt (tartar). It is chiefly used as an addition to the mordant-bath in wool dyeing and for brightening colours on silk after dyeing, and also as a resist and discharge in printing.

SPECIFIC GRAVITY OF TARTARIC ACID SOLUTIONS AT 15° C. (*Gerlach*).

Specific Gravity.	Per cent. $C_4H_6O_6$.	Specific Gravity.	Per cent. $C_4H_6O_6$.
1·0045	1	1·1505	30
1·0090	2	1·1615	32
1·0179	4	1·1726	34
1·0273	6	1·1840	36
1·0371	8	1·1959	38
1·0469	10	1·2078	40
1·0565	12	1·2198	42
1·0661	14	1·2317	44
1·0761	16	1·2441	46
1·0865	18	1·2568	48
1·0969	20	1·2696	50
1·1072	22	1·2828	52
1·1175	24	1·2961	54
1·1282	26	1·3093	56
1·1393	28	1·3220	57·9 (saturated).

Analysis. —The free acid is readily determined by normal caustic soda and phenolphthaleïn.

1 c.c. $\frac{N}{1}$ alkali = 0·075 grm. tartaric acid.

Tartaric acid is sometimes adulterated with bisulphate of potash and alum.

Pure tartaric acid leaves no residue on ignition. H. J. H. Fenton[*] gives the following test for distinguishing it from citric and other acids:—A solution of tartaric acid, or an alkaline tartrate, is treated with a small quantity of ferrous sulphate and two drops of hydrogen dioxide, and finally, excess of caustic potash. A beautiful violet colour is obtained, which in strong solutions is nearly black. The colour is destroyed by chlorine or alkaline hypochlorites, which is not the case with ferrates, which produce a similar reaction.

TARTRAZINE (B.)(S.C.I.). 1884. *Sodium salt of diphenyl p. sulphonic acid oxazone dioxytartaric acid.* Orange-yellow powder. Aqueous solution, golden-yellow; alcoholic solution, bright yellow. Concentrated H_2SO_4, yellow solution, unchanged on dilution.

Application. —An acid colour. Dyes *wool* orange-yellow. Specially fast to light.

TERRA COTTA F (G.). An azo dye.

$$\left.\begin{array}{l}\text{Primuline}\\ \text{Naphthionic acid}\end{array}\right\} \text{Metaphenylene diamine.}$$

1890. Dark brown powder. Aqueous solution, brown. Concentrated H_2SO_4, red-violet solution; on dilution, brown ppt.

Application. —A direct cotton colour. Dyes unmordanted *cotton* terra cotta brown.

TERRA COTTA R (G.) v. ALIZARIN YELLOW R.

TERRA JAPONICA v. CATECHU.

TEXTILE FABRICS (ANALYSIS OF). Although wool, cotton, and silk have certain reactions in common, they may be distinguished from each other chemically.[*] Wool and silk are easily distinguished from cotton by drawing out a thread and setting it on fire. The animal fibres shrivel up and leave a shining, tumefied, difficultly combustible cinder, which yields a large quantity of ash when completely burnt. The smoke smells like burnt horn, and turns turmeric paper brown. The vegetable fibres leave a cinder having the form of the original thread, and only a small quantity of ash ; while they burn with a smoke which has an empyreumatic smell, and reddens litmus. Wool and silk are also easily distinguished from cotton and linen by the yellow colour which they assume when treated with nitric or picric acid, by which the vegetable fibres are not coloured.

Wool and silk also dissolve by boiling with potash or soda lye of specific gravity 1·045, whereas the vegetable fibres remain unchanged. When treated with cuprate of ammonium, cotton, linen, and silk dissolve while wool is insoluble.

Wool and silk can be differentiated from each other by a solution of sodic plumbate, which can be prepared by adding caustic soda to acetate of lead until the resulting

[*] *Chem. News*, vol. xliii., p. 110.

[*] Dr. F. H. Bowman, *Journ. Soc. Dyers and Col.*, 1885, p. 144.

precipitate redissolves. Both wool and hair when treated with this solution turn brown, in consequence of the sulphur which they contain forming dark lead sulphide; while silk which is free from sulphur remains unchanged. It is obvious that this reaction is useful only when the fabric does not contain, besides wool, a notable quantity of *stoved* silk.

Grothe gives the following as the best methods of distinguishing wool and silk* :—

(1) *Wool*, cautiously heated to 130° C., gives off the odour of carbon disulphide and ammonia, assumes a golden-yellow colour and curls up, while silk becomes coloured only at 140° to 145° C., and does not curl up.

(2) When the fibres, moistened with potash lye, are dipped in a solution of cupric sulphate, and then exposed to the air, the *wool* quickly turns brown in consequence of the formation of cupric sulphide, whereas the *silk* remains unchanged.

(3) On mixing a solution of wool in caustic potash with tartaric acid, and then with cupric sulphate, a large quantity of cupric sulphide is formed, and the filtered liquid exhibits a dark brown-red colour. Silk treated in the same manner yields a somewhat viscid solution, having a fine violet colour.

Animal fibres, when heated with Millon's reagent (mercuric and mercurous nitrate), turn red. With *vegetable fibres* this is not the case.

The vegetable fibres (cellulose), as well as silk, are readily dissolved in an ammoniacal solution of copper oxide (prepared, according to Peligot, by dissolving copper filings in ammonia in a current of air), and the former may be precipitated by a number of salts, as well as by sugar or gum, whereas silk can only be separated by means of weak acids.

According to Schlossberger, an ammoniacal solution of protoxide of nickel very easily dissolves silk without attacking cotton.

Liebermann has proposed a very sensitive reaction for the detection of *vegetable fibres* among animal fibres. For this purpose a saturated solution of magenta is prepared, to which caustic potash is added until the solution becomes colourless. The filtered colourless portion of this solution is used for the examination of fibres. The fabric to be tested is dipped for some moments into the liquid, and after withdrawal well washed with water. The effect of this treatment is that the *wool* or *silk* is coloured red, whilst the *cotton fibres* remain altogether colourless.

Persoz finds that *silk* dissolves readily in a hot solution of zinc chloride of 142° Tw.

Rémont has developed the following method:—The sample is boiled for fifteen minutes in a 3 per cent. solution of hydro-

* *Zeitschr. Anal. Chem.*, vol. iii., p. 153.

chloric acid, then washed and dried. The threads of the warp are then separated as far as possible from those of the weft, and examined separately, as mentioned below. A thread is burnt. There is given off a smell like burning horn, and a thread, heated with a fragment of caustic soda, evolves ammonia. In this case some threads are plunged into boiling basic zinc chloride solution. If they dissolve completely the threads are *silk*. If on adding hydrochloric acid to this solution there is a copious flocculent precipitation, the threads are *silk* mixed with *wool* or *vegetable fibres*. If nothing dissolves in zinc chloride the threads are plunged into a boiling 5 per cent. solution of soda. If they dissolve completely wool is present; if partially, wool and cotton. If no odour of burnt horn is given off, the threads consist of *vegetable fibres*. These results may be confirmed by means of the microscope.

For the **Quantitative Examination**, if the preliminary tests show the presence of *silk*, *wool*, and *cotton*, four swatches weighing each 4 grms. are taken, one of which is laid aside.

Determination of the Dressing and Dye.— The swatches are boiled for fifteen minutes in a 3 per cent. solution of hydrochloric acid. If the liquid is deeply coloured it is decanted, and the boiling is repeated with a fresh quantity of acid. The pieces of cloth are then well washed, and dried by wringing them in a piece of linen, and one of them is put aside. In this manner the fabric is freed from size and dressing, and the dye is more or less removed. The colour is thus easily removed from cotton, less readily from wool, and very incompletely from silk. When the latter material is dyed light shades by means of coal-tar colours, the weight of the dye is trifling, and may be neglected. It is not the same if the silk is dyed deep colours, and especially black. An approximate idea of the weighting retained by the tissue may be got by afterwards incinerating a weighed portion of the boiled swatch. If the proportion of oxide of iron remaining is slight, it may be overlooked, but if it reaches 5 to 10 per cent. calculated on the weight of the silk in the cloth it must be taken into account. Two of the pieces, after the treatment with acid and washing, are immersed for one to two minutes in a boiling solution of basic chloride of zinc of 1·72 specific gravity. This is prepared by heating 100 parts of zinc chloride and 4 parts of zinc oxide in 85 parts of water until dissolved. The patterns are allowed to drain and then placed in water, which removes the greater portion of the zinc salt. They are then washed with acidulated water, and eventually in pure water, until the wash water no longer gives a precipitate with ammonium-hydrogen sulphide. By wringing

the patterns after each immersion in a piece of linen, the operation is accelerated, and the silk is thus completely removed. One of the patterns is then laid aside.

Separation of the Wool.—The remaining swatch is gently boiled for a quarter of an hour in a 2 per cent. solution of caustic soda, the loss of water by evaporation being continually replaced by boiling water. In washing and drying the residue it must not be rubbed, lest losses be occasioned by the breaking of the fibres. The four patterns are then dried in a water oven for an hour, and, after taking out, exposed to the air at the same temperature and humidity as on first weighing. The following day the pieces are weighed. The first piece should weigh 4 grms., any difference not exceeding 0·005 grm. may be neglected, but any greater difference must be taken into account. The difference in weight between the first and second patterns gives *size and dressing;* that between the second and third represents the weight of *silk;* that between the third and fourth the weight of *wool;* whilst the weight of the fourth gives the amount of *vegetable fibre* present. Since the vegetable fibre is attacked somewhat by the caustic soda, it is usual to make an allowance of 5 per cent., consequently on adding to the fourth swatch 5 per cent. of its weight we obtain the weight of *cotton.*

Fabrics and yarn, composed of two fibres (cotton and wool, wool and silk, cotton and silk), are much more common than those with three, when, of course, one of the above operations is omitted.

In many cases the *cotton* and *wool* in mixed goods may be determined by carefully separating the weft and the warp threads and weighing the fibres thus obtained. Cotton and woollen fabrics sometimes contain zinc chloride. As is well known, cellulose, when treated with acids, is partly changed into glucose. Starting from this fact, and making use of the colour reactions between glucose and α-naphthol or thymol, Molisch[*] has devised a method of distinguishing vegetable from animal fibres, which in precision leaves nothing to be desired. To avoid all error, the sample under examination must first be boiled several times in water, since for some fabrics gum or saccharine is used as sizing, and these, with naphthol and sulphuric acid, produce colour reactions. If a wool is to be assayed care must be taken that it does not contain burs, &c. The method of proceeding is then as follows:— About 0·01 grm. of fibre, well boiled and washed in plenty of water, is put into a test tube with a little water, two drops of a 20 per cent. alcoholic solution of α-naphthol are added, then concentrated sulphuric acid is poured in, and well shaken. If the

[*] *Ding. Polytec. Journ.*, No. 3, vol. cclxi.

sample contains *vegetable fibres*, the latter are rapidly dissolved, and the liquid, after being shaken, assumes a deep violet colour. If, on the contrary, the fibres are of animal origin, the liquid is coloured a more or less intense yellow, or even brown. If under the same conditions thymol, instead of naphthol, is employed, a coloration between cinnabar and carmine is obtained. Silk behaves with these reagents like the animal fibres. β-naphthol does not give these reactions, and α-naphthol is preferred to thymol, because the reaction is better. It is to be observed that colouring matters do not in any way interfere with this reaction. By noticing in the course of the reaction, the solubility of the different fibres in sulphuric acid, the character of the fibres contained in the fabric may be ascertained. If, for instance, no coloration is produced, which is a sign that the fabric is composed of animal fibres only, the solubility of the latter indicates their origin; silk dissolves very rapidly and completely, while wool dissolves with difficulty. If a coloration takes place, and if the fibres are dissolved completely, the fabric will be of vegetable origin, and may contain, besides, fibres of silk. A coloration, accompanied by an incomplete solution of the fibres, indicates that the fabric contains wool mixed with vegetable fibres.

Although these reactions with α-naphthol are very simple, they cannot by themselves suffice for the assaying of the fabrics, and should be employed only in conjunction with other tests described above.

According to A. Lidoff, *raw silk* dissolves rapidly in melted oxalic acid, *cellulose* dissolves but slowly, while *wool* does not dissolve at all.

For separating *silk* from *cotton* the following solution may be used:—

15 grms. of copper sulphate are dissolved in 150 c.c. of water, 10 grms. of pure glycerin are added, and just sufficient soda to redissolve the precipitate which is at first formed. If the fabric (plush) be heated for twenty minutes in this solution the *silk* is completely dissolved; the *cotton* losing about 1 per cent. of its weight in the process. *Wool* is dissolved to a considerable extent by the copper solution mentioned, hence this method cannot be used in the presence of wool. F. W. Richardson[*] uses for dissolving *silk* a solution of nickel hydrate prepared as follows:—25 grms. of crystallised nickel sulphate are dissolved in about 500 c.c. of water, and the nickel completely precipitated as hydrate by caustic soda; the hydrate is thoroughly washed with water, then rinsed into a 250 c.c. flask with 125 c.c. of water; the flask is then filled to the mark with 0·880 ammonia, and well shaken.

[*] *Journ. Soc. Chem. Ind.*, 1893, p. 430.

This solution dissolves *silk* from fabrics other than plush in two to three minutes in the cold, the losses of *cotton* and *wool* by this treatment being less than 0·5 per cent. In order to dissolve *silk* from *plush* ten minutes' boiling with a reflux condenser is required; in this manner cotton loses nearly 1 per cent.

For the *analysis of plush* it is best to boil the fabric with basic zinc chloride (1·72 sp. gr.), wash with dilute acid and water as mentioned above, dry and weigh the cotton. It is advisable to boil some dyed fabrics with methylated spirit, and finally with ether, to remove certain dyes and oleaginous substances, before treating as above.

Tussur silk, and other wild silks, behave with various reagents differently to mulberry silk. *Ordinary silk* is soon dissolved in a 10 per cent. solution of boiling caustic soda, but *Tussur silk* requires a considerable time.

Tussur silk is only partially dissolved by cold concentrated hydrochloric acid (sp. gr. 1·16), even on standing forty-eight hours, whilst *ordinary silk* dissolves almost instantly. The zinc chloride solution mentioned above, which dissolves mulberry silk readily, only dissolves *Tussur silk* after a considerable time, and then incompletely. Hoehnel gives the following method for the qualitative and quantitative determination of the different silk fibres. If a sample of *mulberry silk* be plunged into a solution of chromic acid saturated in the cold and then diluted with an equal volume of water and boiled for one minute, the silk dissolves completely. Wild silks remain apparently unaltered after boiling for two or three minutes. Wool behaves in this solution like mulberry silk.

In the analysis of all fabrics it is best to take the exact weight of the substance when dried to constant weight, using a stoppered tube both before and at the end of the various treatments, as the fibres are more or less hygroscopic.

Weighted silks are tested as follows by J. Carter Bell*:—5 grms. are dried for the estimation of the *moisture,* then extracted with ether, alcohol, and water, weighing between each solvent. This will give the quantities of *oil, soap, sugar,* and similar compounds added for weighting purposes. Half of the sample is next treated with hydrochloric acid diluted with two volumes of water; the silk is then dried at 230° F. It can then be reduced to powder, which can be mixed with soda lime, and the combustion for nitrogen carried out as usual.

Tin, which is largely used for weighting silks, is detected by heating the silk in strong hydrochloric acid, added in quantity to effect solution, then diluting with water, and passing a current of sulphuretted hydrogen through

Journ. Soc. Chem. Ind., 1897, p. 303.

the solution, when the tin is precipitated as sulphide, and may be further tested in the usual manner.

The *ash* of a genuine silk is about 0·5 per cent., while Tussur silk frequently gives 8 per cent. of ash.

The standard for the amount of nitrogen is pure boiled off silk, dried at the ordinary temperature, which contains 18 per cent. nitrogen.

The following methods of distinguishing artificial silk (nitro-cellulose) from natural silk are recommended by P. Truchot :—*

1. The density of nitro-cellulose is 1·490, that of silk varying from 1·357 to 1·37.

2. When ignited, nitro-cellulose burns without the emission of any acid gases or smell.

3. When treated with Schweitzer's reagent (*q.v.*), nitro-cellulose and silk both swell considerably before dissolving. On the addition of water or hydrochloric acid to the solution obtained from the nitro-cellulose, a white precipitate of cellulose is produced.

4. Nitro-cellulose dissolves in concentrated sulphuric acid with a deep yellow colour, which, on the addition of diphenylamine or of brucine, turns respectively dark blue or red. These colour changes are very characteristic, and are due to the presence in the fibre of nitro-cellulose which has escaped reduction by the compounds with which it has been treated. The test may be made without dissolving the fibre, the latter being simply immersed in a solution of diphenylamine sulphate, when it becomes coloured dark blue, natural silk when similarly treated remaining colourless.

5. A simple test for nitro-cellulose consists in separating the fibres, moistening them with water, and determining their tenacity. The fibres of collodion silk, when moistened, have their outer coating dissolved and become very weak, whilst silk, whether moist or dry, withstands great tensile strain.

Estimation of Water.—The conditioning of textile fibres and fabrics is referred to elsewhere (*v.* CONDITIONING); but it is frequently necessary to operate upon smaller samples of material than are suitable for the apparatus in general use for that purpose. As a rule, it suffices to dry 2 to 3 grms. of the material in a large stoppered tube in the steam-bath until of constant weight. This method generally takes several hours to obtain exact results. The following method, devised by Rawson, gives very good results:—5 to 10 grms. of the yarn or cloth is weighed out and introduced into a thin glass tube of special construction. The body of the tube is about 6 inches in length and 1 inch in diameter. One end is fitted with a ground glass stopper (as in an ordinary filter tube),

Journ. Soc. Chem. Industry, 1898, p. 186.

and the other is connected with a short piece of open tubing about ¼ inch in diameter and 2 inches in length. The stopper is removed and the tube inserted by means of a cork into a tubular water-bath. A current of dry air is drawn through the tube by means of an aspirator, whilst the water in the bath is kept boiling. At the end of forty-five minutes the glass tube with its contents is removed from the bath, the stopper is inserted and the small open end connected by means of a short piece of india-rubber tubing, to a calcium chloride tube. When cold, the tube containing the dry fibre is weighed, the loss in weight being *water*. If desired, the tube may be again heated in a current of air, but it is seldom that a further loss takes place. The operation is completed in a shorter time if a temperature of 105° to 110° be employed instead of that of boiling water. This temperature may be conveniently obtained by using a mixture of glycerin and water. The bath (especially if glycerin or any other substance in addition to water be used) should be provided with an upright condenser. The bath can, of course, be made to accommodate half a dozen or more tubes, if desired.

Estimation of Oil.—Oil and grease in fabrics, &c., are most conveniently determined by extraction with ether or petroleum ether in a Soxhlet apparatus. It is necessary to purify either solvent before using. Small quantities of alcohol if present in the ether will be liable to dissolve off the dye, hence the removal of alcohol from the ether is sometimes advisable. This is effected by shaking out with water. The etherial layer after separation is dried by allowing it to stand in contact with a little solid calcium chloride, and then filtering. In any case the ether or petroleum ether should be distilled from a water-bath, the residue in the distilling flask being rejected.

A. Jawalovski* condemns the use of ether for this purpose, since in the first place it does not dissolve some of the constituents of mineral oils which (mixed with vegetable oil) are often used for oiling wool. Ether is also more liable than petroleum ether to dissolve out soap.

Whichever solvent be made use of, 2 to 5 grms. of the material are taken and introduced into the body of the tube. The lower extremity of the apparatus is connected with a small wide-mouthed flask (previously weighed dry) containing about 60 c.c. of the solvent, and the upper end is connected with an inverted condenser. The flask is arranged to rest on a water-bath, under which is placed a small flame. The heat is so regulated that the ether distils and syphons over into the flask at the rate of about twelve times per

* *Journ. Soc. Dyers and Col.,* 1886, p. 89.

hour. When the extraction is complete, the ether is recovered from the extracted liquid by evaporation, and the flask containing the extract is dried for half an hour in a water-oven, allowed to cool, and weighed. No further loss should ensue on heating for fifteen minutes longer in the oven.

The soap used in scouring yarns and fabrics contains, frequently, rosin and free alkalies. These along with the size, colouring matter, &c., are removed from the material by extracting it (after treatment with petroleum ether) first with hot water, then with a mixture of 2 parts absolute alcohol and 1 part ether. The fabric is then dried at 100° C. and weighed. The loss represents the total amount of the substances detailed above, which were present.

Estimation of Mineral Matter (*Metallic oxides as mordants, &c.*).—The *total mineral matter* is determined by burning 5 to 10 grms. of the material in small portions at a time in a platinum dish and igniting until all the carbon has disappeared. As the ash is usually very light, great care must be taken to prevent any portions being carried away by air currents. The dish, on cooling, is then weighed.

The Qualitative Analysis may be made on small amounts of the fabric in a similar manner, the ash, free from carbon, being treated as follows :—

Chromium Mordants.—Ash, yellowish- or brownish-green. Add a little potassium chlorate and fuse ; a bright yellow mass is obtained. If dissolved in water and acetic acid and acetate of lead added, a yellow precipitate ($PbCrO_4$) is obtained, confirming the presence of chromium. If a trace of chromium is present it may be detected by means of a borax lead, which acquires a green colour in the presence of chromium.

Iron Mordants.—Ash, reddish-brown colour. Dissolve in hydrochloric acid with one drop nitric acid, add potassium ferrocyanide ; a blue precipitate indicates iron.

Copper Mordants (usually occur in combination with iron and sometimes with chromium).—Dissolve the ash in hydrochloric acid, add a slight excess of ammonia and filter. If much copper is present the filtrate will be blue. Smaller quantities are detected by adding acetic acid and potassium ferrocyanide, which produces a reddish-brown precipitate or coloration.

Aluminium Mordants.—Ash, white. Dissolve in hydrochloric acid and add ammonia, which gives a white precipitate in presence of alumina. Confirm by heating on charcoal with cobalt nitrate ; a blue mass is thus obtained.

Tin Mordants.—Ash, white ; yellowish when hot. Small quantities detected by the red colour imparted to a borax lead

containing a trace of oxide of copper when heated in the reducing flame.

The Quantitative Analysis of the Ash of Fabrics.

Estimation of Chromium.—The ash from about 5 grms. of material is mixed with ten to twelve times its weight of a mixture of 2 parts of potassium chlorate and 3 parts of sodium carbonate and fused for twenty minutes in a platinum crucible. On cooling, the mass is treated with hot water and filtered, the residue being well washed with hot water. The filtrate and washings are poured into a porcelain basin, treated with considerable excess of sulphuric acid and a known weight (in slight excess) of *pure* ferrous ammonium sulphate. The excess of ferrous iron is then titrated with $\frac{N}{10}$ potassium bichromate (*v.* POTASSIUM BICHROMATE, ANALYSIS OF). One part of ferrous ammonium sulphate consumed (after deducting excess) = $0.065 \, Cr_2O_3$ or $0.0854 \, CrO_3$

Estimation of Iron and Copper.—If chromium is present, the residue, after fusing and treating with water, is dissolved in hydrochloric acid; in some cases the addition of a little nitric acid is also necessary. The acid solution is diluted with a little water and an excess of ammonia added. The ferric oxide is collected on a small filter, washed a little, re-dissolved in hydrochloric acid and titrated colorimetrically, either with potassium ferrocyanide or thiocyanate (*v.* WATER ANALYSIS).

The *copper* in the filtrate and washings is estimated by "colour titration" in the following manner:—The ammonia is carefully neutralised with acetic acid (a very slight excess of acetic acid is allowable), and the liquid made up to a known volume. A measured volume of the neutralised solution is run into a Nessler glass, half a c.c. of a 5 per cent. solution of potassium ferrocyanide is added, and the liquid diluted to 100 c.c. The depth of shade produced is compared with that given by a standard solution of copper treated in exactly the same manner in another Nessler tube. The copper solution is prepared by dissolving 0·393 grm. of pure crystallised copper sulphate in a litre of water. 1 c.c. of this solution = 0·0001 grm. of Cu.

Detection and Estimation of Arsenic in Textile Fabrics, &c.—The following method, worked out (with modifications) from the papers named below,* can be recommended:— About 15 grms. of fibre, yarn, or cloth are cut up and introduced into a stoppered retort of about 500 c.c. capacity. The neck of the

* A. Atterberg, *Journ. Chem. Soc.*, 1886, *Abs.*, p. 100; Fresenius and Hintz, *Journ. Soc. Chem. Ind.*, 1888, p. 456; *Journ. Soc. Dyers and Col.*, 1888, p. 131; Chittenden and Donaldson, *Chem. News*, vol. xliii. (1881), p. 21.

retort is bent at an obtuse angle, and arranged so that the portion nearest the body points slightly upwards and the bent portion slightly downwards. The retort is connected to a Liebig condenser, the inner tube of which at the extremity farthest from the retort is bent straight down through a cork into a receiving flask capable of holding about 600 c.c. About 50 c.c. of water are placed in the receiver, which is immersed in a basin of cold water. A small set of bulbs (nitrogen bulbs) containing a little water is attached to the flask. 150 c.c. of pure hydrochloric acid are poured into the retort, and after standing an hour, the liquid is distilled down to a small bulk. For this purpose an oil-bath should be used. The retort is allowed to cool, when 25 c.c. more of hydrochloric acid are added and again distilled. The distillate is then made up to 200 c.c., and one-half or one-fourth of the solution treated in a Marsh's apparatus.

For this purpose about 25 grms. of *pure* zinc rods are immersed in a solution of platinum chloride for a few minutes and afterwards well washed with water. The platinised zinc is introduced into a flask of a capacity of 250 c.c., having a horizontal side tube attached to the neck. This is connected to a calcium chloride tube, into which is fixed a piece of hard glass tubing about 12 inches in length and a quarter of an inch in diameter. The hard glass tube is drawn out near the end and bent upwards. The flask is provided with a tapped funnel, through which a little dilute pure hydrochloric acid is poured, and allowed to flow on to the zinc. When the air has been *completely* driven out of the apparatus, the jet is lighted and the hard glass tube (protected with wire gauze) heated to redness for a space of 6 or 8 inches by means of a small furnace of four or five Bunsen burners. An aliquot part of the distillate (50 to 150 c.c.) containing the arsenic in the form of arsenious acid (As_2O_3) is poured into the funnel and allowed to drop regularly into the flask at the rate of about 60 c.c. per hour. Arseniuretted hydrogen (AsH_3) is formed, which, on passing through the red-hot tube with excess of hydrogen, is decomposed and arsenic is deposited. If the amount of arsenic is considerable, a space of 2 or 3 inches should be left between the heated portion and the drawn-out part of the tube. If very small, the tube should be heated close to the drawn-out part so that the arsenic may be deposited in the narrow portion. When the acid liquid containing the arsenic has passed into the flask, 10 to 20 c.c. of pure hydrochloric acid are added and allowed to slowly flow in as before. The tube is then allowed to cool, when the portion containing the deposit of arsenic is cut off with a sharp file and care-

fully weighed on a delicate balance. The arsenic is then removed by simply heating the tube, which, after cooling, is again weighed. The difference between the two weighings gives the amount of arsenic present in the solution. In many cases the arsenic mirror may be too small to weigh, and yet it may represent a considerable amount (comparatively speaking) of arsenic. In such cases the amount of arsenic may be approximately estimated by making experiments with known quantities (very small) of arsenic, and comparing the mirrors obtained. Before commencing the examination for arsenic, it is *absolutely necessary* to make blank experiments with all the substances used in order to ascertain whether they are free from arsenic or not.

*The Testing and Analysis of Finished Goods.**
—If it be desired to know in what manner a cloth has been finished, its physical characteristics are tested, and it will be easy to discover whether the material has been glazed or calender finished. If it be held against the light, it can be found whether it has been weighted, whilst the amount of finish is roughly indicated according as it loses its stiffness by rubbing it between the fingers. By the aid of the microscope it can further be determined whether the starch or finish has only been laid on, or whether it has been made to penetrate into the fibre. The above observations are useful in giving a clue to the nature of the finish.

The determination of the amount of water is useful, inasmuch as an idea of the finish which has been employed can be obtained; it is known that cellulose absorbs less water than starch, and if it be found that the quantity of moisture is comparatively high, it is an indication that the goods have been more or less starched, or contain zinc chloride. In order to estimate the amount of finish contained in a given fabric a sample of 250 square centimetres is cut off and weighed and treated with distilled water containing malt, washed, dried, and weighed again. In some instances it is as well to boil the sample in order to separate out all extraneous matters, but, nevertheless, it is possible that a certain quantity of insoluble soap may be present on the fibre which would not be removed even by washing and boiling, and in this case it would be necessary to pass the material through a boiling dilute acid bath, and, after washing and drying, weigh again. This treatment, if applied to goods which have been dyed, will, in most cases, result in the dye being attacked by the acid. Through these estimations the approximate percentage of finish

* J. Dépierre, *Journ. Soc. Dyers and Col.*, 1889, p. 31.

used can be found, and after that the constituent parts of the latter must be tested, which may be done in two different ways. The material to be tested is treated for several hours with boiling water, by which process *starchy substances, gum, soluble salts*, &c., are removed. The solution thus obtained is filtered and tested for starch with iodine; if any be present a blue coloration is obtained. If no starch be present the solution is concentrated by boiling, and two or three times the volume of alcohol mixed with it, whereby *dextrin* and *gum* are precipitated. *Gelatin* can be detected by means of tannic acid, by which it is precipitated. In order to find out whether the solution contains dextrin or gum, the saccharimeter is made use of; a mixture of the two can, however, be separated by means of a solution of basic lead acetate, as while gum is precipitated in the cold, dextrin is not, whilst both are precipitated on heating. If no precipitate be obtained, and still an organic substance is shown to be present by the saccharimeter, it must be assumed that *moss* or *lichen jelly* was contained in the finish. If *sugar* is present, it is indicated by the hydrochloric acid solution after neutralisation, being precipitated by Fehling's solution. For the testing of the *inorganic* substances which may have been made use of in finishing, the ordinary schemes of analysis must be followed.

The residue remaining on the filter can easily be tested for mineral substances. *China clay* (aluminium silicate) is mostly used for filling and weighting, although *gypsum* and *alabaster* (both sulphates of calcium), or *talc* (hydrated magnesium silicate) are often found.

Resin or *colophony* and *fatty matters* are tested for as mentioned previously (p. 324).

THERMOMETERS and THERMOMETER SCALES. In ordinary thermometers two fixed points are taken—viz., those respectively at which water freezes and boils. In graduating an instrument (after exhausting the tube, filling with mercury, and sealing) the height at which the column of mercury stands at these temperatures is determined by experiment. The space on the tube between these two fixed points is then divided into equal parts, the number of parts being 80, 100, or 180, according to the particular scale employed; and, in order to extend the scale below the freezing point and above the boiling point of water, the equal divisions are continued as far as necessary beyond the fixed points in both directions.

There are three scales in common use—viz., Fahrenheit, Réaumur, and Celsius (Centigrade)—the relationship of which is as follows:—

	Freezing point of water.		Boiling point of water.
Fahrenheit (F.),	32°	.	212°.
Réaumur (R.),	0°	.	80°.
Centigrade (C.),	0°	.	100°.

The following simple formulæ will therefore convert temperatures from one scale into another :—

$$\text{C. to R.,} \quad \text{°R.} = \frac{\text{°C.} \times 4}{5}.$$

$$\text{C. to F.,} \quad \text{°F.} = \frac{\text{°C.} \times 9}{5} + 32.$$

$$\text{R. to C.,} \quad \text{°C.} = \frac{\text{°R.} \times 5}{4}.$$

$$\text{R. to F.,} \quad \text{°F.} = \frac{\text{°R.} \times 9}{4} + 32.$$

$$\text{F. to C.,} \quad \text{°C.} = \frac{(\text{°F.} - 32) \times 5}{9}.$$

$$\text{F. to R.,} \quad \text{°R.} = \frac{(\text{°F.} - 32) \times 4}{9}.$$

THIAMIN YELLOW (Br. S.). A direct cotton yellow produced by the action of *formaldehyde* or *primuline*.

THIAZIN BROWN R (B.). Bronze-black powder. Aqueous solution, brownish-red ; alcoholic solution, brown. Concentrated H_2SO_4, crimson ; on dilution, becomes brown.

Application.—A direct cotton colour. Dyes unmordanted *cotton* reddish-brown.

THIAZIN BROWN G (B.) Similar colour to the above.

THIAZIN RED G (B.). An azo dye from *dehydrothiotoluidin sulphonic acid.* (Primuline.) 1894.

Application.—Similar to THIAZIN RED R.

THIAZIN RED R (B.). 1894. Reddish-blue powder. Aqueous solution, bright red ; alcoholic solution, slightly yellower. Concentrated H_2SO_4, bluish-red ; on dilution, bright red.

Application.—A direct cotton colour. Dyes unmordanted *cotton* bluish-red.

THIAZOL YELLOW (By.). *Clayton yellow* (Cl. Co.), *Turmerine* (Br. S.). An azo dye.

Primuline — Primuline.

1887. Yellow powder, soluble in water or alcohol. Concentrated H_2SO_4, brownish-yellow solution ; on dilution colour becomes paler.

Application.—A direct cotton colour. Dyes unmordanted *cotton* bright yellow.

THICKENERS. All those substances which are employed in calico-printing with the object of increasing the viscosity of the liquid containing the colouring matter are known by the name thickeners. Their use prevents the colour solution from running and causes it to remain on that portion of the material where it was originally placed until the colour is dry. As a rule, those thickeners which are used solely for the purpose of increasing the viscosity of the colour solution should be soluble in water in order to allow of their ready removal by washing.

British Gum. DEXTRIN.

Preparation. — Dextrin is obtained by heating starch paste to 60° C. with diastase for ten minutes, then cooling, filtering, boiling, and concentrating to a thick syrup. This liquid consists of dextrin and maltose ($C_{12}H_{22}O_{11}$). A similar product results by treating starch ($C_6H_{10}O_5$) with dilute acids, but the resulting body has a slight acid reaction. On evaporation to dryness the mixture forms an uncrystallisable solid.

British gum has a similar composition to the above-mentioned substance, but is prepared by the action of heat on starch. The starch is first dried and then heated from 212° to 275° C.

Properties.—According to the depth of colour of the "calcined farina," as it is sometimes called, three grades of the product are distinguished—viz., light, medium, and dark British gum. All these varieties contain more or less unaltered starch, the dark gum containing the least.

Dextrin gives a red colour with iodine, *starch* produces a dark blue colour.

The deep colour of the "dark gum" renders it unsuitable for most purposes. The "medium gum" is the most generally used material.

Light British gum is useful on account of the large amount of starch present, which under the influence of caustic soda (as used in printing indigo by the process of Schlieper and Baum) is converted into a viscous substance, having considerable thickening properties.

British gum is also used for dressing crape, lace, &c.

Dextrin causes the cloth when finished to have a particularly soft feel, due to the complete removal of the thickener by washing, hence it is employed in the printing of wool, unions, and silk.

Analysis of Commercial Dextrins.—Starch is detected qualitatively by treating the cold dextrin solution with just so much alcohol as produces a slight turbidity. The dilute alcoholic solution is then warmed until the turbidity disappears, and tannic acid added. On cooling, all the starch is precipitated in thin flakes. The precipitate is well washed with alcohol on a filter, dried, and tested by adding a drop of dilute iodine solution to the residue. If starch be present a blue coloration of the particles will result.

The following determinations may also be required :—1. Starch. 2. Dextrin. 3. Maltose. 4. Ash. 5. Moisture. 6. Acidity.

Water is determined by drying at 105° C.

Ash is found by incinerating a few grms.

Starch is the portion insoluble in cold water.

Dextrin and *Maltose.* — 25 grms. of the sample are treated with cold water, transferred to a 500 c.c. flask, made up to the mark, allowed to stand some time, and filtered. 50 c.c. of the filtrate on evaporation and drying gives the amount of dextrin, sugar (maltose), and soluble salts. The latter can be determined by ignition of the residue.

Maltose is estimated gravimetrically by adding a few c.c. of the filtrate to 40 c.c. of Fehling's solution and 60 c.c. boiling water. Boil twelve minutes, filter and wash the cuprous oxide, dry and ignite to cupric oxide. The weight of CuO obtained multiplied by 0·743 gives the weight of *maltose.*

The percentage of total soluble matter, less the soluble ash, after subtracting the maltose, gives the percentage of *dextrin.*

Should the amount of insoluble matter (starch) be large, an allowance for its volume must be made. If we accept the figure 1·6 as the specific gravity of starch, the number of c.c. to be deducted from the 500 c.c. of solution will be—

$$\frac{\text{Wt. of starch in grms. in 25 grms. sample}}{1\cdot6}.$$

If the percentage of starch be 40, the volume to be deducted will be 6·2.

The *acidity* is determined by titrating 50 c.c. of the filtrate with $\frac{N}{10}$ caustic soda and phenolphthaleïn.

The following figures show the general composition of commercial dextrin:—Dextrin 54; starch 35; maltose 10; water 0·5; ash 0·5; acidity 25 c.c. $\frac{N}{10}$ NaOH.

Gum Arabic, *Gum Acacia,* occurs as an exudation on the stems and branches of several species of *Acacia* found in Africa. Its specific gravity when dried at 15° C. is 1·487. It is soluble in both cold and hot water, the temperature making only a slight difference. The thickening capacity of the gum is not much affected by acids. A solution of basic lead acetate causes the gum to be precipitated from its aqueous solution. This gum differs from gum tragacanth (*q.v.*).

Gum Arabic occurs in commerce as rounded lumps of a nearly white appearance. The lumps are very brittle, and when broken present a vitreous fracture. The ash on calcination is about 3 per cent., consisting of carbonates of calcium, magnesium, and potassium. Gum Arabic is employed chiefly for reserve or resist colours, China clay being generally added to increase the viscosity and protect the fibre from the colour. Indian gum arabic is of a dark colour, and insoluble in water.

The following is a delicate test for the detection of *dextrin* in gum arabic:—Add to 60 c.c. of water 15 drops of a potassium ferricyanide solution, 15 drops ferric chloride solution, and 5 drops of dilute hydrochloric acid of 1·165 specific gravity. Add 3 c.c. of this reagent to a 20 per cent. solution of the gum to be tested. If the gum is pure a clear yellow coloration ensues, which does not alter in from eight to ten hours. If dextrin be present, the colour alters and within three hours becomes blue.

Gum Senegal is closely allied to gum arabic, being also obtained from a species of *Acacia* growing in northern Africa. It is much darker in colour than gum arabic and, unlike that substance, its surface is free from cracks. Colours thickened with gum senegal give very solid shades.

Both gum arabic and gum senegal are sometimes used in solution for thinning starch thickenings which have been made more viscous than is required.

Gum Tragacanth exudes from the stems of *Astragalus gummifer.* It is found in Greece, Turkey, Syria, and Persia. Another name for this substance is "Gum Dragon." It is sent into the market in the form of thin, flat, yellowish-white pieces. It is translucent, and of a horny character. When water is added to the gum one portion dissolves and the remainder swells up considerably, the whole on mixing forming a thick mucilage. H. Koechlin states that it becomes completely soluble on heating for four hours at 80° to 100° C. with hydrogen dioxide in water. Gum senegal may be distinguished from gum arabic, in that it gives a clear solution with borax, and that it does not give a precipitate with sodium stannate or silicate.

If alkalies be present the whole of the gum is soluble in water.

Gum tragacanth possesses great thickening power, and is used together with starch paste for thickening all kinds of "starch colours."

An analysis of the gum gave the following results:—Moisture, 19 per cent.; soluble gum, 35 per cent.; insoluble gum, 43·25 per cent.; ash, 2·75 per cent.

G. Lunge[*] has devised an arrangement for determining the viscosity of gums, &c. It consists of a kind of hydrometer, which is placed on the surface of the thickening (made by treating 750 grms. of dry gum with 1 litre of water for twenty-four hours), and noting the time which it requires to sink to a certain point. The determinations must be carried out at 15° C.

THIOCARMINE R (C.). A thiazine derivative. *Sodium salt of diethyl dibenzylthionin disulphonic acid.* 1890. Indigoblue powder or paste very soluble in water, slightly in alcohol. Concentrated H_2SO_4, grass-green solution; on dilution, bright blue.

[*] *Journ. Soc. Dyers and Col.,* 1896, p. 12.

Application.—An acid colour. Dyes *wool* or *silk* bright blue from an acid bath. A substitute for indigo carmine.

THIOCATECHIN (P.). A sulphide colour. *Action of sulphur and sodium sulphide on para diamines.* 1894. Greyish-black hygroscopic lumps; soluble in water, insoluble in alcohol. Soluble in alkalies. Concentrated H_2SO_4, brownish-red solution; on dilution the colour is precipitated.

Application. — Dyes unmordanted *cotton* fast yellowish-brown shades from an alkaline bath containing sodium sulphide.

THIOCATECHIN S (P.). Produced by action of alkaline sulphites on above. Used in calico printing.

THIOCHROMOGEN (D.) *v.* PRIMULINE.

THIOCYANIC ACID *v.* CHROMIUM SULPHOCYANIDE.

THIOCYANOSIN (Mo.). An eosin dye. *Tetrabrom thio dichlorfluoresceïn methyl ether.*

THIOFLAVIN S (C.). A primuline derivative. *Sodium salt of methylated primuline.* 1888. Yellow powder easily soluble in water. Alcoholic solution yellow with green fluorescence. Concentrated H_2SO_4, brownish-yellow solution; on dilution, orange-yellow precipitate.

Application.—A direct cotton colour. Dyes unmordanted *cotton* bright canary yellow.

THIOFLAVIN T (C.). A primuline derivative. *Dimethyl primuline methyl chloride.* 1888. Yellow crystalline powder. Aqueous or alcoholic solution yellow, the latter with green fluorescence. Concentrated H_2SO_4, colourless solution, becoming yellow on dilution.

Application.—A basic dye. Dyes tannin-mordanted *cotton* yellow, unmordanted *silk* yellow with green fluorescence.

THIONINE *v.* LAUTH'S VIOLET.

THIONINE BLUE G O EXTRA (M.) (Ber.). *Zinc chloride double salt of dimethyl ethyl thionine.* 1885. Reddish-brown powder. Aqueous or alcoholic solution blue. Concentrated H_2SO_4, yellowish-green solution; on dilution becomes blue.

Application.—A basic colour. Dyes tannin-mordanted *cotton* blue.

**THIOPHLOXIN** (Mo.). An eosin dye. *Tetrabromthio dichlor fluoresceïn.*

THIOPHOSPHINE *v.* CHLORAMINE YELLOW.

THIORUBIN (D.). An obsolete azo acid red.

THIOSULPHATE OF SODA *v.* SODIUM THIOSULPHATE.

TIN, $Sn = 117 \cdot 5$.

Preparation.—The most important ore of tin is *tinstone* (SnO_2). For the separation of the metal the ore is roasted, ground with coal, and the mixture heated in furnaces—

$$SnO_2 + 2C = Sn + 2CO.$$
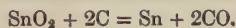
The crude tin is purified by melting at a low temperature, the metal being run off, and thus separated from iron, &c.

Properties.—Tin is a bluish-white metal, having a crystalline structure. It is fairly soft, ductile, and malleable. Its specific gravity is 7·3, and its melting point 228° C. When heated strongly it takes fire, and forms stannic oxide (SnO_2.).

Concentrated hydrochloric acid dissolves tin with evolution of hydrogen—

$$Sn + 2HCl = SnCl_2 + H_2.$$

Tin is violently attacked by nitric acid, nitrous fumes being given off and meta-stannic acid formed.

On boiling tin with caustic soda, sodium stannate is produced—

$$Sn + 2KOH + H_2O = K_2SnO_3 + 2H_2.$$
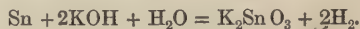
Tin undergoes very little alteration in the air, and owing to its not being readily attacked by acids, &c., is used as a lining for dye vats in silk dyeing.

Tin forms two series of salts—viz., stannous and stannic compounds.

Stannous salts result from the action of hydrochloric or sulphuric acids on the metal or on stannous hydrate. These compounds are colourless, and dissolve in water, showing an acid reaction to litmus, and having a metallic taste. They are strong reducing agents and absorb oxygen from the air.

Neutral or acid solutions of stannous salts yield a brown precipitate of stannous sulphide SnS when treated with sulphuretted hydrogen.

Stannous Acetate, $Sn(C_2H_3O_2)_2$. — Tin crystals in dilute acetic acid solution are treated with lead acetate whereby a colourless liquid is obtained containing the salt in solution. Dilution or heating causes immediate dissociation of the solution. It is employed in calico printing as a resist and discharge.

Stannous Chloride, $SnCl_2 + 2H_2O$.—*Tin crystals, Tin salt.*

Preparation.—Granulated tin is dissolved in hot hydrochloric acid and the solution evaporated. Crystals having the above composition separate from the liquid. If the solution be not crystallised it is sold as *single muriate of tin* (60° Tw.) and *double muriate of tin*, which is double the strength of the first-mentioned solution—viz., 120° Tw. The composition of these liquids varies considerably, and they are sometimes adulterated. An excess of hydrochloric acid prevents formation of basic chlorides on keeping the solutions.

Properties.—Stannous chloride forms colourless monoclinic crystals, which melt at 40° C. and become anhydrous at 100° C.

An anhydrous stannous chloride ($SnCl_2$) can be prepared by the action of dry hydrochloric acid on heated tin. It is a white solid, which melts at 250° C. and can be distilled without decomposition.

The crystals are very soluble in water; the solution becomes turbid on the addition of much water, owing to the separation of tin oxychloride—

$$SnCl_2 + H_2O = SnCl(OH) + HCl.$$

The undiluted solution deposits the same substance on standing in air—

$$3SnCl_2 + H_2O + O = 2SnCl(OH) + SnCl_4.$$
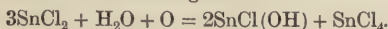
This basic salt is dissolved on the addition of hydrochloric acid.

When the crystals are exposed to air they oxidise similarly to the solution.

Stannous chloride is largely used in dyeing, and it also enters into the composition of other mordants.

Analysis of Stannous Chloride.—Stannous chloride is occasionally found adulterated with zinc or magnesium sulphates or zinc chloride.

Sulphates may be readily detected by addition of hydrochloric acid and barium chloride.

Zinc and magnesia may be detected in the filtrate, after precipitating the tin as sulphide, by the ordinary methods of analysis.

Estimation of Tin.—About 0·25 grm. of the sample is dissolved in a little water containing hydrochloric acid and mixed with 50 c.c. of a 10 per cent. solution of Rochelle salt (potassium sodium tartrate) and 50 c.c. of a 10 per cent. solution of sodium bicarbonate. A little starch solution is then added and the liquid titrated with $\frac{N}{10}$ iodine until a permanent blue colour appears.

1 c.c. of $\frac{N}{10}$ iodine = 0·0059 grm. of Sn. Fairly good results may also be obtained by simply dissolving the "tin crystals" in dilute hydrochloric acid and titrating direct with $\frac{N}{10}$ iodine.

Indirect Estimation by Permanganate.—0·5 grm. is dissolved in water and hydrochloric acid. A slight excess of ferric chloride is then added, which oxidises the tin to stannic chloride, becoming itself reduced to ferrous chloride. The liquid is diluted with recently boiled and cooled water and titrated with $\frac{N}{10}$ potassium permanganate, each c.c. of which corresponds to 0·0059 grm. of Sn.

Solutions of stannous chloride contain the same impurities (as well as free sulphuric acid) as may be present in tin crystals.

Estimation of Stannous Chloride. — The amount of tin present as stannous chloride may be estimated either by $\frac{N}{10}$ iodine or by ferric chloride and $\frac{N}{10}$ permanganate, as described above.

If *stannic chloride* is also present, which is frequently the case, the total amount of tin is estimated by allowing a piece of pure metallic zinc to remain in a weighed portion of the sample for ten or twelve hours. If 25 c.c. of the sample are diluted to 500 c.c., 25 c.c. of this solution will be a convenient amount to take. The tin, which is thus entirely precipitated in the metallic form, is carefully collected and washed, and dissolved in hydrochloric acid with the aid of platinum foil. This should be done in a flask in a current of carbon dioxide to prevent oxidation. The stannous chloride solution obtained is then titrated as above.

Estimation of Free Acid.—Since stannous chloride has an acid reaction to indicators, the free hydrochloric acid present cannot be titrated direct. In order to ascertain the amount of free acid present, it is necessary to determine the total acid (free and combined), and to calculate the amount required to combine with the percentage of tin found. For this purpose W. Minor * recommends that 10 c.c. of the solution be diluted with water, and the tin precipitated as sulphide by a current of sulphuretted hydrogen. The filtrate is made up to a litre, and 500 c.c. boiled, to expel hydrogen sulphide, and titrated with a solution of soda. It is quite unnecessary, however, to separate the tin. The total acid may be accurately estimated by titrating the solution of stannous chloride direct with caustic soda and phenolphthalein. The stannous hydrate formed has no action whatever upon the indicator. If pure stannous chloride is titrated in this way, the exact amount of combined acid is obtained.

Example.—25 c.c. of a solution of single muriate of tin = 30·88 grms. were diluted to 500 c.c.

25 c.c. required 21·8 c.c. of $\frac{N}{10}$ iodine = 8·33 per cent. of Sn.

50 c.c. of the diluted solution (= 3·088 sample) with phenolphthalein required 19·8 c.c. of normal caustic soda.

1 c.c. normal soda = 0·0365 grm. of HCl.

$$\therefore \frac{0·0365 \times 19·8 \times 100}{3·088} = 23·40 \text{ °/}_0 \text{ of HCl free and combined.}$$

8·33 parts of Sn require 5·15 parts of HCl to form $SnCl_2$.

$$\therefore 23·40 - 5·15 = 18·25 \text{ °/}_0 \text{ of free HCl.}$$

Stannous Hydrate, $Sn(OH)_2$.—Stannous hydroxide is precipitated as a white powder on the addition of sodium carbonate to a stannous salt.

* *Chem. News*, vol. lxiii. (1891), p. 249, from *Zeitsch. angew Chemie.*

$$SnCl_2 + Na_2CO_3 + H_2O$$
$$= Sn(OH)_2 + 2NaCl + CO_2.$$
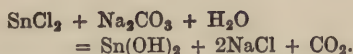
Caustic potash and soda dissolve the precipitate, but it is insoluble in ammonia. If the precipitate be boiled with potash it is resolved into metallic tin and potassium stannate, K_2SnO_3. In the stannates, tin acts as an acid.

Stannous hydroxide is a weak base. It dissolves in acids forming stannous salts.

Stannous Nitrate, $Sn(NO_3)_2$.—This salt is unknown in the free state.

Preparation. — A solution of stannous nitrate is obtained by treating stannous hydroxide or metallic tin with dilute nitric acid.

$$4Sn + 10HNO_3$$
$$= 4Sn(NO_3)_2 + 3H_2O + NH_4NO_3.$$
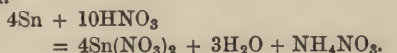
One part of grain bar tin is slowly dissolved in 8 parts of nitric acid (32° Tw.); the latter should be free from the lower oxides of nitrogen. If the reaction be too violent the tin forms metastannic acid, which is useless for mordanting purposes. The solution, which has a strength of about 60° Tw., is of a deep yellow colour, and deposits a white precipitate on long standing.

Stannous nitrate is used by woollen dyers in the production of cochineal scarlets under the names, *Scarlet spirits, Bowl spirits,* &c.

Stannous Oxalate, SnC_2O_4.—This substance is formed as a white powder on adding oxalic acid to stannous chloride solution. In mordanting wool with the above mixture the white precipitate which is formed at first, disappears. Mixtures of tin spirits containing oxalic acid are sometimes used.

Stannous Oxide, SnO. — Stannous oxide may be prepared as a black powder by heating stannous hydroxide in an atmosphere of carbon dioxide. When heated in air it takes fire and oxidises to stannic oxide (SnO_2).

Stannous oxide dissolves in acids, forming stannous salts. Potash and soda dissolve it with production of stannites.

STANNIC SALTS are compounds in which stannic hydroxide acts as a base. They are colourless, soluble in water, and have a disagreeable taste. Acid and neutral solutions form, with ammonium sulphide, a yellow precipitate of stannic sulphide (SnS_2), which is soluble in alkaline sulphides. Sodium sulphate, ammonium nitrate, and most neutral salts of the alkalies precipitate stannic hydroxide from the aqueous solutions if not too acid.
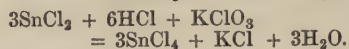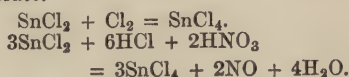
Stannic Acetate, $Sn(C_2H_3O_2)_4$, is used in calico printing in the form of a solution prepared by mixing concentrated solutions of stannic chloride and lead acetate. An addition of 1 part of acetic acid to every 2 parts of crystallised lead acetate is required to prevent dissociation on boiling.

Stannic Chloride, $SnCl_4$.

Preparation.—Anhydrous stannic chloride is formed when a current of chlorine is passed over heated tin. It is a colourless liquid, which fumes strongly in the air, and boils at 114° C. It combines with water with evolution of heat; the hydrates, $SnCl_4 + 3H_2O$, $SnCl_4 + 5H_2O$, $SnCl_4 + 8H_2O$, are known. On boiling, the solution decomposes with precipitation of metastannic acid and liberation of hydrochloric acid.

$$SnCl_4 + 3H_2O = H_2SnO_3 + 4HCl.$$
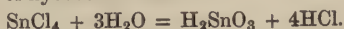
On the large scale stannic chloride is prepared by the oxidation of stannous chloride solutions by means of chlorine or by hydrochloric acid and nitric acid or potassium chlorate.

$$SnCl_2 + Cl_2 = SnCl_4.$$
$$3SnCl_2 + 6HCl + 2HNO_3$$
$$= 3SnCl_4 + 2NO + 4H_2O.$$
$$3SnCl_2 + 6HCl + KClO_3$$
$$= 3SnCl_4 + KCl + 3H_2O.$$

The oxidation by means of potassium chlorate yields a good product. 10 lbs. of tin crystals are dissolved in 3½ gallons of boiling water, and 13 lbs. of hydrochloric acid (25° Tw.) are added; 18 lbs. of potassium chlorate are then added in small quantities at a time. The product will be turbid if too little hydrochloric acid be present. The liquid has a yellow colour and smells of chlorine. On cooling, the smell should have disappeared, otherwise a little stannous chloride must be added to neutralise the chlorine. A double salt of stannic chloride and potassium chloride will crystallise from the solution if insufficient water be used. The temperature must not be allowed to rise too high during the reaction.

Specific Gravity.	Per cent. $SnCl_4+5H_2O$.	Specific Gravity.	Per cent. $SnCl_4+5H_2O$.
1·012	2	1·366	50
1·024	4	1·386	52
1·036	6	1·406	54
1·048	8	1·426	56
1·059	10	1·447	58
1·072	12	1·468	60
1·084	14	1·491	62
1·097	16	1·514	64
1·110	18	1·538	66
1·124	20	1·563	68
1·137	22	1·587	70
1·151	24	1·614	72
1·165	26	1·641	74
1·180	28	1·669	76
1·195	30	1·698	78
1·210	32	1·727	80
1·227	34	1·759	82
1·242	36	1·791	84
1·259	38	1·824	86
1·276	40	1·859	88
1·293	42	1·893	90
1·310	44	1·932	92
1·329	46	1·969	94
1·347	48	1·988	96

Stannic chloride is sold in monoclinic crystals, $SnCl_4 + 5H_2O$, or as an aqueous solution. The table on p. 331 gives the specific gravity and strength of solutions of pure stannic chloride ($SnCl_4 + 5H_2O$) at 15°, according to Gerlach.

Diluted solutions of stannic chloride dissociate on long standing only; on boiling, stannic hydroxide is precipitated at once—

$$SnCl_4 + 3H_2O = H_2SnO_3 + 4HCl.$$
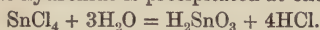
Stannic chloride combines with many chlorides, forming crystalline compounds—*e.g.*, $SnCl_4 + 2SCl_4$ and $SnCl_4 + PCl_5$. With the chlorides of the alkali metals it forms crystalline double salts.

Stannic chloride is an important mordant for silk.

Analysis of Stannic Chloride.—Solutions of stannic chloride, consisting of stannic chloride only, or of mixtures of this salt with stannous chloride, are used under various names. Acids other than hydrochloric acid, such as sulphuric, nitric, and oxalic, are also frequently present. The liquid known as *solution of tin* sold at about 44° Tw., and containing about 8 per cent. of tin, usually consists of stannic chloride only, with a slight excess of hydrochloric acid and a little nitric acid. If any *stannous* chloride is present a drop of the liquid will produce a white or grey precipitate, with a solution of mercuric chloride.

Estimation of Tin.—The amount of tin may be determined by precipitation with zinc, as already described; or by the following gravimetric process, which gives very accurate results:—About 5 grms. of the solution are diluted with water to 200 c.c., and, if any stannous salt be present, a weak solution of iodine is added, until the liquid is faintly yellow. A dilute solution of ammonia is now gradually added, until a faint opalescence appears; when an excess of a concentrated solution of sodium sulphate is added. The liquid is kept hot on the water bath for one or two hours, and the somewhat voluminous precipitate washed two or three times by decantation. It is then collected on a filter, thoroughly washed, dried, ignited, and weighed as SnO_2.

150 parts of SnO_2 = 118 parts of Sn.

Free acid is determined in stannic chloride solutions by means of caustic soda and phenolphthaleïn in the same manner as in solutions of stannous chloride. In calculating the combined acid four equivalents of hydrochloric acid must be taken instead of two.

Besides a chemical analysis, dye trials with the solution should always be made. The exact method of dyeing the swatches will depend upon the purpose for which the mordant is required.

Pink Salt, $SnCl_4 + 2NH_4Cl$.—This substance is a double salt of stannic chloride and ammonium chloride, which crystallises from a mixture of the salts in aqueous solution. The salt is stable in the air and soluble in water. The diluted solution deposits stannic oxide on boiling; the concentrated solution is not dissociated by heat.

"Pink salt" was formerly used by calico printers, but stannic chloride is now generally used in its stead.

Stannic Hydroxide, H_2SnO_3—*Stannic acid.*—On the addition of ammonia to a solution of a stannic salt, or on treating sodium stannate with an acid, a white precipitate of stannic acid is deposited. It is readily soluble in concentrated hydrochloric and nitric acid, and also in caustic alkalies. Water dissolves the substance slightly, the aqueous solution being acid to litmus. On dissolving stannic hydroxide in acids stannic salts are formed. Although in the stannic salts it acts as a weak base, it has still more pronounced acid properties. The compounds in which stannic hydrate acts as an acid are called stannates. The soluble stannates have an alkaline reaction, and are decomposed by the carbon dioxide of the air, stannic hydroxide being precipitated.

Metastannic Acid (H_2SnO_3).—This substance is a white powder, formed by treating tin with nitric acid and warming the mixture. Metastannic acid is liable to be formed whenever tin is acted on by nitric acid if the acid be strong or the temperature high, hence great care is necessary in preparing tin mordants to prevent the formation of this substance. Metastannic acid is devoid of mordanting properties.

Stannic Nitrate is produced when stannic hydroxide is dissolved in nitric acid; the solution coagulates on heating to 50° C.

Stannic Oxalate, $Sn(C_2O_4)_2$.—Oxalate of tin is made by dissolving stannic hydroxide in oxalic acid solution on the steam bath. It is soluble in water, the solution becoming turbid in the air. Stannic oxalate is used in calico printing for the production of alizarin reds, &c.

Stannic Oxide, SnO_2, occurs as the mineral *tinstone*. It is prepared artificially by roasting tin in the air. Stannic oxide is a white amorphous powder which is insoluble in alkalies and in acids. It forms stannate of soda on melting with caustic soda.

Stannic Sulphate is formed by dissolving stannic hydroxide in sulphuric acid. On evaporating the solution it is obtained as a white mass.

Stannic Sulphide, SnS_2.—On heating a mixture of tin filings, sulphur and ammonium chloride, a crystalline golden-yellow mass is produced called "mosaic gold," which consists of stannic sulphide.

Stannic Sulphocyanide, $Sn(CNS)_4$.—*Thiocyanate of tin* is obtained by dissolving

stannic hydroxide in sulphuric acid, and treating the solution with barium sulphocyanide. The diluted solution can be boiled without decomposition. Stannic thiocyanate is employed in calico printing.

Stannate of Soda, Na_2SnO_3—*Sodium stannate, Preparing Salt.*

Preparation.—Sodium hydrate and sodium nitrate are melted together and feathered tin added with continual stirring. The mixture deflagrates, becomes white hot, and forms a mass of sodium stannate. The commercial product contains sodium carbonate and chloride; sodium arsenate and sodium tungstate are sometimes added to increase the effect of the salt.

Properties.—Stannate of soda is a white crystalline solid, soluble in about twice its weight of cold water. It crystallises with 3, 8, 9, or 10 molecules of water. Sodium stannate has mild caustic properties. It is decomposed by the carbon dioxide of the air, with formation of carbonate of soda and stannic acid (H_2SnO_3).

Uses.—Sodium stannate is used as a mordant in dyeing and printing, the goods being first impregnated with a solution of the salt and subsequently passed through dilute sulphuric acid, hydrated stannic oxide being precipitated on the fibre. The value of sodium stannate depends upon the amount of tin it contains; this varies from 8 to 20 per cent.

Sodium Stannite, Na_2SnO_2, is prepared by melting tin with an equal weight of caustic soda, with constant stirring. A solution of this substance is used in dyeing and printing.

Tin Spirits.—The term "Tin spirits" is applied to tin mordants generally, but more particularly to solutions of stannous salts, which are employed chiefly in wool dyeing. "Tin spirits" are prepared, as a rule, by dyers themselves who make the mixtures, according to the particular formula which practice has shown to yield certain results. The introduction of the artificial dyestuffs has diminished the importance of these compounds. The substances named *yellow, orange, scarlet, amaranth, purple, plum,* and *puce spirit* are prepared by adding sulphuric acid to stannous chloride solution, or treating tin with a mixture of sulphuric and hydrochloric acids. *Red, purple,* and *aniline spirit,* or *nitromuriate of tin* are obtained by dissolving tin in a mixture of hydrochloric and nitric acid. They are essentially mixtures of stannous chloride and nitrate, with more or less stannic nitrate and chloride. *Scarlet finishing spirit* contains oxalic acid, and sometimes tartaric acid also.

Cotton spirits consist for the greater part of stannic salts. Sodium chloride, ammonium chloride, sodium nitrate, bisulphate of potash, and other salts are often added with doubtful benefit.

Such mordants are used for cotton under the names *oxymuriate of tin, crimson, barwood, plum, red cotton, purple,* and *cotton spirits, pink cutting liquor,* &c.

TINCAL *v.* SODIUM BORATE.

TIN CRYSTALS *v.* TIN (STANNOUS CHLORIDE).

TIN RED LIQUOR *v.* ALUMINIUM ACETATE.

TIN SALT *v.* TIN (STANNOUS CHLORIDE).

TIN SPIRITS *v.* TIN (STANNOUS CHLORIDE).

TIN STONE *v.* TIN (STANNIC OXIDE).

TINTOMETER *v.* COLORIMETERS.

TITAN BLUE 3 B and R (H.). Direct cotton dyes (*v.* below).

TITAN BROWN O, Y, R (H.). Mark Y. Brown powder. Aqueous solution, reddish-brown; alcoholic solution, rather redder. Concentrated H_2SO_4, bluish-red solution; on dilution, brown ppt., which re-dissolves on further dilution.

Application.—Direct cotton dyes. Give yellowish (O) and reddish (Y and R) shades on unmordanted *cotton.*

TITAN COMO G, R, S (H.). Mark R. Reddish-blue powder, slightly soluble in water; easily in alcohol with bright blue colour. Concentrated H_2SO_4, bluish-red solution; on dilution, bright blue.

Application.—Direct cotton dyes, giving bright blue shades.

TITAN GREY (H.). Direct cotton colour.

TITAN NAVY B, R (H.). Mark R. Violet-black powder, soluble in water with a violet colour; slightly soluble in alcohol with reddish-blue colour. Concentrated H_2SO_4, bright blue; on dilution, reddish-blue.

Application.—Direct cotton dyes, giving bluish and reddish navy blues.

TITAN PINK 3 B (H.). *Titan pink.* Brownish-red powder. Aqueous solution, bright bluish-red, slightly soluble in alcohol with light red colour. Concentrated H_2SO_4, bluish-red; on dilution, red ppt.

Application. — A direct cotton colour, giving bluish-pinks.

TITAN RED FOR WOOL (H.). Reactions same as TITAN PINK.

Application. — A direct cotton colour. Specially suitable for wool.

TITAN SCARLET C, S (H.). *Titan scarlet.* Dark red powder. Aqueous solution, yellowish-red; alcoholic solution, orange. Concentrated H_2SO_4, bluish-red; on dilution, orange-red.

Application.—Direct cotton dyes. Mark C dyes yellowish- and Mark S bluish-scarlets.

TITAN YELLOW G G, G, R, Y (H.). *Titan yellow R.* Brownish-yellow powder. Aqueous solution, bright yellow; alcoholic solution, brownish-yellow. Concentrated H_2SO_4, orange-red solution; on dilution,

brown ppt., which re-dissolves on further dilution.

Application.—Direct cotton dyes Mark G G gives greenish-yellows, R dull reddish-yellows, Y intermediate shades.

TOLAN RED (K.) An acid colour.

TOLEDO BLUE V (L.). Direct cotton colour. May be fixed with metallic salts.

TOLUENE, TOLUOL, C_7H_8, occurs in coal tar. It is closely allied to benzene (*q.v.*). Its specific gravity is 0·872 at 15° C., and its boiling point 111° C.

TOLUIDINE BLUE O (B.) (M.) (Ber.). A thionine colour. *Zinc chloride double salt of dimethyl toluthionine.* 1888. Dark green powder. Aqueous solution, blue-violet; alcoholic solution, blue. Concentrated H_2SO_4, yellowish-green solution; on dilution, blue.

Application.—A basic colour. Dyes tannin-mordanted *cotton* blue.

TOLUIDINES, $C_6H_4(CH_3)NH_2$. Three isomeric toluidines are known, which strongly resemble aniline; they may be obtained by the reduction of three different nitro-toluenes. By the action of nitric acid on toluene, chiefly ortho- and paranitro-toluene are obtained, which yield on reduction a mixture of ortho- and paratoluidine. (*v.* also ANILINE.)

Orthotoluidine is a colourless oil which boils at 197° C., and has a specific gravity of 1·0037 at 15°.

Metatoluidine is a colourless oil which boils at 197° C. It occurs in small quantities only in the commercial products, and has no practical value owing to its high cost.

Paratoluidine forms colourless crystals, which melt at 45° C. and boil at 198° C.

Analysis.—*v.* ANILINE (ANALYSIS OF).

TOLUYLENE BLUE B (O.). A basic induline. 1889. Brownish-violet powder, soluble in water with an indigo-blue colour. Concentrated H_2SO_4, blue solution; on dilution, no change.

Application.—Dyes tannin-mordanted *cotton* indigo-blue. Will also dye unmordanted cotton.

TOLUYLENE BROWN (O.) (By.). An azo dye.

Naphthionic acid

Toluylene diamine ⟩ *Metaphenylene diamine.*
sulphonic acid ⟨ *Metaphenylene diamine.*

Naphthionic acid

1889. Black-brown powder. Aqueous solution, brown; insoluble in alcohol. Concentrated H_2SO_4, dirty reddish-violet solution; on dilution becomes brown.

Application.—A direct cotton colour. Dyes unmordanted *cotton* brown.

TOLUYLENE BROWN G (O.) (By.). An azo dye.

Toluylene diamine — Phenylene diamine.

1890. Blackish-brown powder. Aqueous solution, brown; insoluble in alcohol. Concentrated H_2SO_4, brownish-red solution; on dilution becomes brown.

Application.—A direct cotton colour. Dyes unmordanted *cotton* brown.

TOLUYLENE DIAMINE, $C_6H_3(CH_3)(NH_2)_2$. Largely used as a developer in dyeing with direct cotton dyes. Frequently called "diamine."

TOLUYLENE ORANGE G (O.) (By.) (Ber.). An azo dye.

Tolidin ⟨ *Cresotic acid.*
⟨ *Metatoluylene diamine sulphonic acid.*

1888. Yellowish-red powder, with bluish cast. Aqueous solution, brownish-yellow; Concentrated H_2SO_4, magenta-red solution; on dilution, brown ppt.

Application.—A direct cotton colour. Dyes unmordanted *cotton* orange.

TOLUYLENE ORANGE R (O.). An azo dye.

Tolidine ⟨ *Metatoluylene diamine sulphonic acid.*
⟨ *Metatoluylene diamine sulphonic acid.*

1888. Brownish-red powder, giving an orange solution in water. Concentrated H_2SO_4, brown solution; on dilution, red ppt.

Application.—As TOLUYLENE ORANGE G.

TOLUYLENE ORANGE 2R (O.). An azo dye.

Toluylene diamine ⟨ *Beta-naphthylamine.*
sulphonic acid ⟨ *Beta-naphthylamine.*

1891. Red powder. Aqueous solution, yellowish-red; alcoholic solution, orange. Concentrated H_2SO_4, bluish-green solution; on dilution becomes brownish-red, then precipitates, and on further dilution re-dissolves.

Application.—*v.* TOLUYLENE ORANGE G.

TOLUYLENE RED *v.* NEUTRAL RED.

TOW *v.* FLAX.

TRAGACANTH *v.* THICKENERS.

TRAM *v.* SILK (REELING).

TRIACETIN *v.* ACETIN.

TRIAMINE BLACK B, BT (S.C.I.). Direct cotton blacks, suitable for diazotising and developing.

TRIPHENYL ROSANILINE *v.* SPIRIT BLUE.

TRISULPHON BLUE B, R (Sandoz). Direct cotton blues.

TRISULPHON BROWN G, GG, and TRISULPHON VIOLET. Direct cotton colours.

TRONA *v.* SODIUM CARBONATE.

TROPAEOLIN D *v.* ORANGE III.

TROPAEOLIN G (C.) *v.* METANIL YELLOW.

TROPAEOLIN O (C.) *v.* RESORCIN YELLOW.

TROPAEOLIN O O (C.) *v.* ORANGE IV.
TROPAEOLIN O O O No. 1 *v.* ORANGE I.
TROPAEOLIN O O O No. 2 *v.* ORANGE II.
TROPAEOLIN O O O O. An obsolete azo acid orange.
TROPAEOLIN R *v.* RESORCIN YELLOW.

TUNGSTEN. *Wolfram.* $W = 184$. Tungsten occurs in combination with iron and oxygen as the ore *Wolframite*. The metal is prepared by heating the trioxide, WO_3, with carbon. It is a bright grey metallic powder, which burns in air forming the trioxide. The latter compound dissolves in carbonates of the alkalies and in ammonia, forming *tungstates*. If a solution of an alkaline tungstate be acidified, *tungstic acid* in the form of a white precipitate, $H_2WO_4 + H_2O$, is thrown down.

Sodium Tungstates.—A number of sodium polytungstates are known besides the normal salt, $Na_2WO_4 + 2H_2O$. Sodium tungstate is prepared by fusing the mineral Wolframite with carbonate of soda and lixiviating the mass, evaporating the extract, and crystallising. The sodium salt crystallises in rhombic tables, soluble in 4 parts of cold or in 2 parts of hot water. The aqueous solution has an alkaline reaction and a bitter taste.

Sodium Paratungstate, $Na_{10}W_{12}O_4$, is prepared similarly to the normal sodium salt from *Wolframite*, $FeMnWO_4$. This substance crystallises generally with 28 molecules of water.

The tungstates of soda have been successfully used in the preparation of uninflammable textile materials, for which purpose it is especially appropriate, owing to the fact that the colours are unaffected and the fibres not attacked.

Attempts have been made to substitute sodium tungstate for stannate of soda with doubtful success.

According to Camille Schoen * wool which has been boiled with tungstate of soda has very little affinity for acid colours, but will dye in darker shades with the basic colours than ordinary wool. Sodium tungstate has also found application in the weighting of silk, for which purpose, owing to its high specific gravity, it is well adapted.

When a solution of sodium tungstate and glue is acidified a peculiar combination is formed, which has been proposed as a substance for precipitating on cotton, in order to animalise the fibre or make it more receptive to dyes.

Tungstate of Chromium, $Cr_2(WO_4)_2$, is formed by acting on chrome alum with an alkaline tungstate. Chromium tungstate in the form of a green paste containing about 40 per cent. of dry matter is used as an oxidising agent in aniline black printing.

* *Journ. Soc. Dyers and Col.*, 1893, p. 130.

TURKEY-RED OIL. *Alizarin oil, Sulphated oil, Soluble oil* or *Olein.*

Preparation.—Sulphuric acid is slowly run into castor oil with continual agitation during a period of about eighteen hours. From 20 to 40 parts of sulphuric acid are required for 100 parts of oil. The temperature must be maintained below 40° C. or a dark and unsatisfactory product will result. A small quantity of sulphur dioxide is always evolved, probably due to the reduction of the sulphuric acid by the mucilaginous substances present. After standing some time a sample is poured into distilled water, to which has been added a few drops of ammonia. If it yield a clear solution the product must be washed immediately, as decomposition soon commences. The mass is agitated with a solution of sodium sulphate or brine to remove excess of free acid. Eventually the oil is partially neutralised with sodium carbonate or ammonia and diluted with water if required. Olive oil and cottonseed oil are sometimes substituted for castor oil, but the resulting product is inferior to the castor-oil preparation.

Properties.—Turkey-red oil consists for the greater part of two compounds, one of which is very *soluble* in water and consists of *ricinoleic sulphate*, produced as follows:—

$$C_{18}H_{33}O_2 . OH + H_2SO_4$$
Ricinoleic acid.

$$= C_{18}H_{33}O_2 . O . SO_3H + H_2O.$$
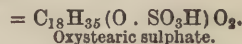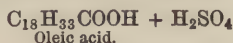Ricinoleic sulphate.
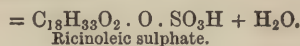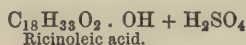
This substance is very stable in the cold, and forms about two-thirds of the mixture; it is soluble in water in all proportions and lathers like soap.

The *water insoluble* portion of castor Turkey-red oil is chiefly *free ricinoleic acid*, together with small amounts of *unchanged oil*. This portion is soluble in the predominating part of the mixture. Small quantities of polymerised bodies are also probably present.

Ricinoleo-sulphuric acid is not decomposed on boiling its aqueous or alkaline solutions, but on boiling with dilute hydrochloric acid it is decomposed into sulphuric acid and ricinoleic acid.
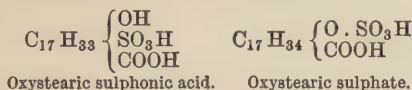
According to *Benedikt*, castor Turkey-red oil cannot be replaced by other oils, for the reason that by treating them with sulphuric acid, *saturated* hydroxy acids and their sulphuric acid ethers are formed, thus (taking oleic acid as an example)—

$$C_{18}H_{33}COOH + H_2SO_4$$
Oleic acid.

$$= C_{18}H_{35}(O . SO_3H)O_2.$$
Oxystearic sulphate.

The oxystearic sulphate is then decomposed for the greater part as follows:—

$$C_{18}H_{35}(OSO_3H)O_2 + H_2O$$
Oxystearic sulphate.

$$= C_{18}H_{35}(OH)O_2 + H_2SO_4.$$
Oxystearic acid.
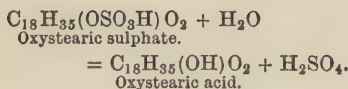
Consequently Turkey-red oil from olive, arachis, cottonseed oil, and oleic acid contains *saturated* acids, castor Turkey-red oil consists solely of *unsaturated* fatty acids. Turkey-red oil is not a true sulphonic acid; it belongs, according to its whole behaviour, to the class of sulphuric ethers. The difference of constitution is made apparent by the two following formulæ for sulphated oil from olive oil :—
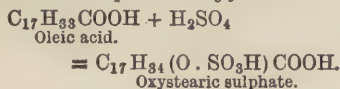
$$C_{17}H_{33}\begin{cases}OH \\ SO_3H \\ COOH\end{cases} \qquad C_{17}H_{34}\begin{cases}O . SO_3H \\ COOH\end{cases}$$

Oxystearic sulphonic acid.   Oxystearic sulphate.

R. Benedikt [*] and F. Ulzer have shown that the soluble part of a Turkey-red oil produced from olive oil consists principally of oxystearic sulphate (*v.* above), while a Turkey-red oil from castor oil contains ricinoleic sulphate :—

$$C_{17}H_{32}(OH)COOH + H_2SO_4$$
Ricinoleic acid.

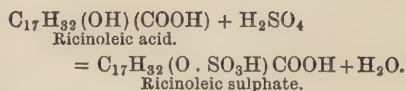$$= C_{17}H_{32}(O . SO_3H)COOH + H_2O.$$
Ricinoleic sulphate.
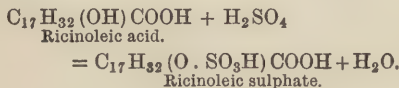
To show this, the true sulphonic acid of a higher fatty acid was first prepared by an entirely different method, in order to ascertain whether the compounds belonging to this group of bodies behaved similarly to the Turkey-red oil acids soluble in water. The compound, which could not be obtained in the pure state, is in many respects similar to the Turkey-red oil acid, but the two are essentially different from each other in their behaviour with hydrochloric acid : the sulphonic acid is not decomposed by concentrated hydrochloric acid, even at a high temperature ; while the acid from olive Turkey-red oil is easily decomposed, even by dilute hydrochloric acid, into sulphuric acid and oxystearic acid.

Ricinoleic acid, $C_{17}H_{32}(OH)(COOH)$, differs essentially from oleic acid, $C_{17}H_{33}(COOH)$, inasmuch as it contains a hydroxyl group in addition to the carboxyl group.

When sulphuric acid acts on ricinoleic acid or triricinolein (castor oil), it does not form a sulphate by addition, as is believed to be the case with oleic acid, triolein, &c., but the H of the hydroxyl group is replaced by the group SO_3H, *a true etherification taking place with the separation of water, and a non-saturated compound being formed* :—
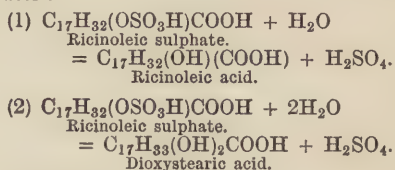
$$C_{17}H_{33}COOH + H_2SO_4$$
Oleic acid.

$$= C_{17}H_{34}(O . SO_3H)COOH.$$
Oxystearic sulphate.

[*] *Journ. Soc. Dyers and Col.*, 1888, p. 44.

$$C_{17}H_{32}(OH)(COOH) + H_2SO_4$$
Ricinoleic acid.

$$= C_{17}H_{32}(O . SO_3H)COOH + H_2O.$$
Ricinoleic sulphate.

The Turkey-red oil from castor-oil has therefore a far greater capability of oxidation than the olive Turkey-red oil, and is consequently a better mordant than the latter, a fact of great importance in dyeing, especially in Turkey-red dyeing.

The ricinoleic sulphate may lose its sulphuric acid with or without the addition of water :—

(1) $C_{17}H_{32}(OSO_3H)COOH + H_2O$
Ricinoleic sulphate.
$= C_{17}H_{32}(OH)(COOH) + H_2SO_4.$
Ricinoleic acid.

(2) $C_{17}H_{32}(OSO_3H)COOH + 2H_2O$
Ricinoleic sulphate.
$= C_{17}H_{33}(OH)_2COOH + H_2SO_4.$
Dioxystearic acid.

The decomposition of the ricinoleic sulphate proceeds principally according to the first equation and results in the formation of ricinoleic acid, which is disposed to polymerise and oxidise.

According to Juillard and Scheurer-Kestner,[*] castor Turkey-red oil contains the sulphuric ethers of ricinoleic acid and of several polyricinoleic acids mixed with the products of their decomposition, among which ricinoleic acid predominates. Glycerin is always present in the commercial oil.

P. Lochtin (*l. c.*) considers the ordinary Turkey-red oil as a mixture of (insufficiently neutralised) sulpho-fatty acids and fatty acids; he ascribes only a subordinate importance to the sulpho-compounds in Turkey-red oil. Lochtin prepared an acid ammonium ricinoleate having approximately the formula $(NH)_4C_{18}H_{31}O_3$, $C_{18}H_{34}O_3$, and obtained in experimental dye trials with this so-called *acid soap*, a more even, fuller, and purer shade than in dyeing with the Turkey-red oil. The reasons why castor-oil soap (with soda), now frequently applied instead of Turkey-red oil, produces inferior results are to be found in the fact that the solution of the soap is much more frothy than that of the neutralised sulphated oil ; and chiefly because the dyed material shows the flat and dirty shade of the alkaline alizarate. This last fact is explained by the suggestion that in mordanting with alumina a waterproof envelope—ricinoleate of alumina—is formed externally on the fibre, thus enclosing the nucleus of alkali soap. As good results as with Turkey-red oil were obtained with the soap solution by modifying in the first place the method of clearing, which was continued (after boiling under pressure) with weak solutions of the lime salts (gypsum,

[*] *Journ. Soc. Dyers and Col.*, 1891, p. 69.

calcium chloride, calcium nitrate, &c.) ; in order to avoid the injurious influence of the soda as much as possible, Lochtin added sulphuric acid so as to neutralise one-half to three-fourths of the alkali present (which did not separate the fatty acid from the solution). He further prepared the above-mentioned ammoniacal oil soap, and found that material oiled with this soap contains little alkali after drying, and in the alkaline clearing produces results not inferior to those obtained with Turkey-red oil. There is some difference between the Turkey-red oil and the acid soap. The material prepared with ammoniacal Turkey-red oil shows an acid reaction after drying, the ammonium salt being decomposed and the sulpho-fatty acid producing sulphuric acid; while, on the other hand, the material oiled with the ammoniacal oil soap shows, after drying, a neutral or faintly alkaline reaction.

Turkey-red oil is heavier than water ; it is very soluble in water, forming a solution with an acid reaction, and is precipitated unchanged by sodium sulphate. If allowed to stand for several days in contact with water at the ordinary temperature it does not decompose at all ; hence it is more stable than generally supposed. On boiling with twice its weight of water it becomes milky at first, but subsequently separates completely into an aqueous liquid, and an oil which floats at the top. The supernatant liquid is entirely free from mineral acid ; all the latter being in the aqueous layer.

When Turkey-red oil is dissolved in ether, and water is added to the etherial solution, the latter becomes milky and gives a white precipitate. This reaction has been attributed to a decomposition of the substance dissolved by the ether ; but, on the addition of more water, the precipitate re-dissolves, forming a clear syrupy liquid, which, on addition of sulphate of soda, yields the unchanged sulphated fatty acid, while the ether contains non-sulphated fatty acid.

Scheurer-Kestner is of opinion that the sulphated compound, when dissolved in water, exists in the hydrated state, containing 16·4 per cent. of water. Dehydration takes place when it is dissolved in ether, and, on addition of water, an insoluble anhydrous compound is precipitated at first, which, however, becomes soluble by hydration. Turkey-red oil, as it comes into commerce, or as it is obtained by the previous method, is, according to this author, always hydrated.

The non-sulphated portion is very acid and must be either ricinoleic acid or a polymerised derivative. It is lighter than, and insoluble in water, is free from the elements of sulphuric acid, is easily soluble in caustic soda, and is precipitated without alteration by sulphuric acid. The other part of the oil is heavier

than water, in which, however, it dissolves, giving a perfectly clear solution without fluorescence. Fluorescence only exists when the soluble and insoluble oil are re-united ; in this case the light oil dissolves in the other, and communicates this property to it. The soluble oil contains the elements of sulphuric acid in the proportion corresponding to 8·5 per cent SO_3. It dissolves in caustic soda, and is precipitated by sulphuric acid without alteration. It is strongly hydrated, and when dehydrated at a gentle heat it thickens until it acquires about the consistency of wax. Precipitated from its aqueous solution by sulphate of soda, it is combined with 30 to 40 per cent. water, which it gradually loses on being heated to 75° C. ; towards 80° C. it colours slightly, becomes turbid, and loses 5 to 6 per cent. more water. A solution of the water-soluble sulphated oil in water, although stable at the ordinary temperature, decomposes within a few hours at 80° C., while the light oil is not affected by heat.

As to the brightening properties of the two substances, they are remarkable for their difference ; for whilst the insoluble oil imparts to alizarin pink a crimson, the soluble oil gives it a yellow shade.

The percentage of unmodified oil depends both on the temperature and on the quantity of acid which have been employed in sulphating. On the large scale, the amount of acid used never suffices to sulphonate the whole quantity of castor oil, a large excess being required to attain this end. Theoretically, nearly 1 part of sulphuric is required for 3 parts castor oil ; and this may be further reduced by one-third, since one-third of the product is not sulphated. But in practice, even smaller quantities of sulphuric acid are used, and a considerable amount of what is used is not taken up in the process. From our present knowledge on the subject, we may consider the commercial Turkey-red oil as a mixture of ricinoleic sulphate, ricinoleic acid, and unmodified castor oil ; possibly products of polymerisation, sulphated glycerin ethers, dioxystearic acid, and other compounds are also present.

Uses.—Turkey-red oil is used in Turkey-red (alizarin red) dyeing, as a mordant for basic colours in cotton dyeing, for preparing calico before printing, and in the finishing of cotton goods. Its alkaline solution acts like a soap and is sometimes used as such.

The Examination and Analysis of Turkey-red Oil.—A good sample should not show any appearance of oily drops on diluting with ten times its volume of tepid water, even after standing some hours. No turbidity ought to appear on diluting the oil with a considerable amount of aqueous ammonia. A turbidity indicates the presence of solid fats, and proves that in the manufacture of the article either

22

very impure castor oil or other crude oils (rape, sesame, cottonseed, olive, and train oils), or mixtures of these have been used, all of which contain palmitin and stearin.

An alcoholic solution of Turkey-red oil is the more turbid, the more unaltered oil it contains.

Estimation of Total Fatty Matter.—This determination is of considerable importance, and is carried out by Breinl[*] as follows :—A flask of 200 c.c. capacity, having a long neck and graduated to $\frac{1}{10}$ c.c., is required. 30 grms. of the sample are accurately weighed off and washed into the flask with hot water, the volume made up to about 100 c.c., then 25 c.c. of sulphuric acid of specific gravity 1·56 are added, and the mixture heated to boiling, with frequent shaking until the fatty matter forms a clear and transparent layer. A hot concentrated solution of common salt is next added in small portions until the separated layer of fat rises above the lowermost mark. After cooling, the volume is read off, the number of c.c. multiplied by 3 corresponds to the percentage of total fatty matter.

J. A. Wilson[†] has devised the following method for estimating the total fatty matter :—10 c.c. of saturated salt solution are run into a globular separator, and 5 to 6 grms. of the sample poured into the separator. About 5 c.c. HCl (1 : 1) are then added, and the whole thoroughly agitated with 25 c.c. ether ; the acid solution is run off and again treated in another separator with 25 c.c. more ether, and after separating from the aqueous layer it is added to the first ether extract. The ether is then evaporated and the fatty matter in the flask dried by blowing air through for about ten minutes. 30 c.c. of absolute alcohol are then added, the solution agitated and allowed to stand for a short time, poured through a dry filter, the residue in the flask washed three times with alcohol, and all received through the filter into a tared flask ; the alcohol is evaporated and the fatty acids dried on the water-bath about an hour, whilst a current of air is passed through the flask. The residue is then weighed and the percentage calculated.

Neutral Fat.—Benedikt and Lewkowitsch[‡] proceed as follows :—About 30 grms. of the sample are dissolved in 50 c.c. of water, 20 c.c. of ammonia and 30 c.c. of glycerin are added, and the mixture exhausted with ether twice, using 100 c.c. each time. The etherial solution is freed from small quantities of dissolved soap by washing with water, and transferred to a tared wide-mouthed flask. After evaporating the ether, the residue is dried at first on the water-bath, then in an air-bath at 100° C., and weighed.

Soluble Fatty Acids (Sulphonated Fatty Acids).—About 10 grms. of the oil are dissolved in a stoppered bottle in 25 c.c. of water, 25 c.c. of fuming hydrochloric are added, and the bottle is heated in an oil-bath to 140° C. for one hour. Water is added after cooling, the mixture transferred to a beaker, and the fatty layer filtered off through a moistened filter, and the fat washed with hot water into a 250 c.c. flask. After cooling, the liquid is run through a dry filter to eliminate any particles of fat, and 208 c.c. of the filtrate treated with barium chloride. From the amount thus found, after multiplying by five-fourths, the quantity of sulphuric acid, as determined in the following test (see below), is subtracted, and the difference calculated to ricinoleic acid, 80 parts of SO_3, corresponding to 378 parts of ricinoleo-sulphuric acid, $C_{18}H_{33}O_2 . O . SO_3H$. The molecular weight of hydroxystearo-sulphuric acid being 380, the calculation will remain the same, even if other oils were used in the preparation of the Turkey-red oil.

Sulphuric Acid.—The quantity of sulphuric acid present in the form of ammonium or sodium sulphate, is found by dissolving a weighed quantity of the sample in ether, and shaking it several times with a few c.c. of saturated salt solution (free from sulphate). The whole of the washings are united, diluted, filtered, and the filtrate precipitated with barium chloride.

Ammonia and Caustic Soda.—10 grms. of the sample are dissolved in a little ether, and extracted four times with dilute sulphuric acid (1 : 6), using 5 c.c. each time.

For the determination of *ammonia* the acid liquors are distilled with caustic potash, and the vapours absorbed in a measured quantity of standard acid ; after titrating back the excess of acid, the amount of ammonia is calculated.

For the estimation of *caustic soda* the acid liquors are concentrated in a platinum dish on the water-bath, and the excess of sulphuric acid driven off by heating on the sand bath ; the residue is mixed with ammonium sulphate, ignited, and the residue of sodium sulphate weighed.

Iron is determined, according to Emde,[*] by shaking up a quantity of the oil in a graduated cylinder with dilute sulphuric acid. A few drops of potassium ferrocyanide are added, and the whole shaken up with a little ether. The oil dissolves in the ether, and forms a sharply-defined layer on the water. If iron be present, a more or less dense layer of Prussian blue, containing all the iron, will appear at the line of contact of the two liquids. If in comparative tests the same quantities of oil, water, acid, and potassium ferrocyanide be used, the density

* *Journ. Soc. Chem. Industry*, 1889, p. 573.
† *Ibid.*, Jan., 1891.   ‡ *Oils, Fats, and Waxes.*

* *Journ. Soc. Chem. Ind.*, 1888, p. 591.

of the coloration will show roughly the amount of iron present. For accurate determinations the iron is precipitated with ammonia as hydrate, and weighed as ferric oxide.

The ash may be estimated by burning a quantity of the oil at a low temperature in a platinum basin, and weighing the residue. The amount ranges from 0·1 to 0·3 per cent.

Bensemann recommends taking the *melting point of the fatty acids*, after treating the oil with dilute hydrochloric acid, shaking out with ether, washing out the excess of hydrochloric acid, evaporating off the ether, and drying the residue, which consists of fatty acids and unaltered oil. This gives a good idea as to the nature of the oils used for manufacturing the Turkey-red oil, even if mixtures are present. Thus the melting point of the mixture of fatty acids from cottonseed oil lies between 42 to 43° C., from olive oil 26 to 27° C., from rape oil 21 to 22° C. ; whilst the castor-oil acid remains liquid below 0° C.

The fatty acids from Turkey-red oil made from pure castor oil, give a clear solution, even after considerable dilution with alcohol. But a mass of fatty acids separated from other oils yields with alcohol a turbid solution, ultimately separating into drops of oil on the surface, consisting of unchanged triglycerides.

A dyeing trial may be made by treating two similar pieces of cotton with a 5 per cent. solution of the sample and with a standard oil of similar strength for half an hour. After drying, mordanting with alum, and dyeing with alizarin (blue shade) or printing with steam red, the samples are brightened and finished as usual.

TURMERIC — *Origin.* — This dyestuff, which has also been called *Indian saffron,* is the tuber or underground stem of the *Arnomum curcuma,* or of various species of *Curcuma,* chiefly *Curcuma tinctoria,* a plant which grows chiefly in India, China, Japan, and the East Indies. It has been employed as a dyestuff for several hundred years.

Two principal varieties are distinguished— viz., *Rotunda* and *Longa,* the former being potato-shaped masses, and the latter having an irregular spindle-shaped appearance. Externally the tubers are drab or yellowish-grey in colour, but internally they are deep yellow or brownish-orange.

When ground, turmeric forms a light, bulky, resinous powder, which possesses a powerful aromatic smell and taste; and, in addition to its use as a dyestuff, it is largely used as a condiment in curries, &c. The roots, particularly when ground, should be stored in a dry place, since if moist, the colouring matter is somewhat rapidly destroyed.

Colouring Matter.—The colouring matter of turmeric is almost insoluble in cold water, but dissolves slowly in hot water. It is easily soluble in alcohol, ether, or alkaline solutions. It was first isolated in a pure state by Vogel and Pelletier, who named it *Curcumin;* but its exact composition is uncertain, being variously stated as follows :— $C_{10}H_{10}O_3$ (*Daube*), $C_{16}H_{16}O_4$ (*Gajewsky*), $C_{14}H_{14}O_4$ (*Jackson*); while the latest observers (*Ciamician* and *Silber*) assign to it the formula $C_{19}H_{14}O_4(O . CH_3)_2$ (*Ber.*, 1897, vol. xxx., p. 182).

It may be prepared by digesting the ground roots with carbon bisulphide to remove turmeric oil and resinous and other impurities, and then extracting the colouring matter by means of a dilute solution of caustic soda. The dark brown alkaline liquid, on neutralisation with hydrochloric acid, yields a yellow precipitate of impure curcumin, which is dried and crystallised from ether. It forms pale yellow prismatic crystals, which melt at 178° C.

Turmeric oil is an unsaponifiable oil, existing in turmeric to the extent of about 10 per cent. of its weight. Its composition is uncertain, but on oxidation it yields, amongst other products, terephthalic acid, $C_6H_4(COOH)_2$, a derivative of benzene.

Turmeric is extremely sensitive to alkalies, which impart to it a deep reddish-brown colour. Paper saturated with an alcoholic solution of turmeric and dried, is frequently employed in testing liquids for the presence of alkalies, which cause it to turn brown.

The most characteristic reaction of turmeric is that with boric acid. A piece of filter paper is immersed in the solution in which turmeric is suspected and then dried at a gentle heat. It is then moistened with boric acid solution and again dried, when it acquires a brownish-red colour, which is turned green on addition of a trace of caustic soda.

Application of Turmeric.—Turmeric dyes all fibres without the aid of a mordant, and is thus one of the very few natural substantive dyes. It is still employed in dyeing compound shades on wool, usually in conjunction with *orchil* and *indigo extract,* but frequently also along with acid coal-tar dyes. It is rarely used on silk.

TURMERINE (Br.S.) *v.* THIAZOL YELLOW.

TURNBULL'S BLUE *v.* PRUSSIAN BLUE.

TURPENTINE. Oil of turpentine is used by printers in mixing many colours, to prevent frothing or "flurrying," and give uniformity of composition. The most frequent adulterants are petroleum oils. These oils at once lower the boiling point very considerably, the normal boiling point being 160° C. By fractionating the product distilling over below 160° C., and determining its specific gravity, which will, in case petroleum or

shale naphthas have been added, be lower than that of turpentine, and by testing its behaviour towards chlorine and nitric acid, the presence of petroleum oils may be detected. The specific gravity of oil of turpentine is 0·890. If petroleum oils were present the specific gravity of the turpentine would be reduced, as the specific gravity of the adulterants does not exceed 0·710. The residue on evaporation of a small quantity of turpentine on a watch-glass should not be oily.

Turpentine is also used for mixing with albumen and for cleaning machines.

TUSSUR *v.* SILK.

TWADDELL'S HYDROMETER *v.* HYDROMETER.

TYRALIN *v.* ROSOLAN.

TYRIAN PURPLE. The date of the discovery of this substance is uncertain, but Pliny, who describes and often refers to it, gives the approximate time as 1400 B.C., "when Minos reigned in Crete."

Tyrian, or Laconian, purple was obtained from certain shellfish which attach themselves to rocks on the sea coast between low and high watermarks.

Several varieties of shellfish appear to have been used, the two most valued being known as *Buccinum* and *Purpura*. The secret of the method of producing the colour was jealously guarded by the few who were initiated, but appears to have been somewhat as follows :—The colour-producing liquid exists in certain glands in a colourless condition, and these being extracted were laid in salt for a few days. The glands were then macerated to a pulp, and boiled gently in a leaden vessel for several days, the impurities which rose to the surface being skimmed off from time to time. Wool could then be dyed in this liquid, the colour being intensified by subsequent exposure to light. Wool dyed with Tyrian purple was very costly, 1 lb. weight being worth £40 of our money.

The particular shade of purple obtained, depended upon the way in which the dye was prepared, that most closely resembling amethyst being esteemed above all others. From an early date, however, other dyestuffs were used in conjunction with the shellfish purple with the two-fold object of modifying and cheapening the colour. In this connection we find the first mention of orchil, the *Fucus marinus* referred to by Pliny, probably being a purple dye obtained from such lichen. Kermes (*Coccus ilicis*) and alkanet root (*Anchusa tinctoria*) were also made use of for this purpose.

All knowledge of the method of producing Tyrian purple appears to have entirely disappeared between 1100 and 1200 A.D., and it remained a lost art throughout the Middle Ages. It was re-discovered by an English chemist (Cole), who found, about the end of the seventeenth century, certain shellfish on the coast of Somersetshire which were capable of yielding a purple colour. These were afterwards shown to be *Buccinum*. The only use made of the colour at this time was for marking linen, and Cole's process, which is described in vol. xv. of the *Phil. Trans. of the Royal Society*, 1685, was simply to paint the linen with the colourless liquid from the glands before referred to, and then expose to sunlight. A remarkable series of colour changes then occur. "The letters or marks will presently appear of a pleasant green colour, and in a few moments will change to a full sea-green, after which it will alter to a watchet blue ; from that, in a little time more, it will be of a purplish-red, after which, in an hour or two, it will develop into a very deep purple, beyond which the sun can do no more."

The matter was further investigated by the French chemist, Réaumur, who in the main corroborated Cole's results, and a full account of his interesting experiments is given in the *Memoirs de l'Academie Royale des Sciences*, &c., Paris, 1711. Twenty years later Duhamel found the *purpura* in great abundance on the coast of Provence, and also succeeded in producing the purple (*Ibid.*, 1736).

Bancroft, from whose *Philosophy of Permanent Colours*, London, 1813, most of the above notes are taken, also made very original experiments in 1803, and proved that light was the essential agent in developing the colour changes described by Cole, the purple being readily produced *in vacuo* under the action of strong sunlight.

There is little doubt that the purple produced by Cole, Réaumur, Duhamel, and Bancroft was identical with the old Tyrian purple, but its re-discovery did not lead to its re-introduction into the dyeing industry, because the use of the much cheaper and more easily obtainable orchil had become general.

Colours closely allied to, if not identical with, Tyrian purple are still in use amongst certain coast tribes in South America, and possibly other countries.

The chemical composition of Tyrian purple has never been determined, but it is not improbable that it is allied to the *alloxan* of Liebig and Wöhler, which is produced by the action of nitric acid upon uric acid. When treated with ammonia, alloxan produces a beautiful purple colour known as *murexide*, which in 1855-56 was largely employed in calico printing. Its discovery was, however, too late to be of much practical use, and the introduction of the coal-tar dyes a few years later led to its entire abandonment. During the time it was in use, the large quantities of uric acid required in its manufacture were obtained from Peruvian guano.

U

UNION BLACK B, 2 B (B.). Direct cotton colours, specially suitable for wool-cotton unions.

UNION BLACK S (C.). Direct cotton colour, specially suitable for wool-cotton unions.

UNION FAST CLARET (Lev.) *v.* ORCHIL RED A.

UNSAPONIFIABLE MATTER DETERMINATION *v.* LUBRICATING OILS (ANALYSIS OF).

URANIA BLUE (D.). 1896. Bluish-violet powder, with bronzy lustre. Aqueous solution, blue. In concentrated H_2SO_4, brownish-green solution ; on dilution, blue solution.

Application.—An acid colour. Dyes *wool* and *silk* blue from an acid bath.

URANIN (B.) (Ber.) (L.) (M.) (Br.S.) *v.* FLUORESCEÏN.

URANIUM, U = 239. This metal occurs in various minerals in the form of oxide, *pitchblende*, UO_2, $2UO_3$, being one of the most important. In many respects uranium resembles chromium. The metal itself is of only minor importance. The salts of uranium are poisonous.

Uranium acetate, $UO_2(C_2H_3O_2)_2 . 2H_2O$, is made by gently heating the nitrate of the metal, and treating the residue with acetic acid at a moderate temperature, and crystallising.

Uranium nitrate, $UO_2(NO_3)_2 . 6H_2O$, occurs in the form of yellow rhombic crystals. It is prepared by dissolving the oxides of uranium in nitric acid. Its use as a mordant in calico printing has been suggested.

Uranium sulphate, $U(SO_4)_2 + 8H_2O$, has been suggested as a mordant for wool.

W. M. Gardner,[*] who has experimented with this salt (which crystallises in rhombic crystals of a green colour), finds that with alizarin red, fine grey shades may be obtained.

URINE is secreted by the kidneys from the arterial blood ; it contains in solution a part of the nitrogenous waste of the animal organism in the form of *urea* $CO \begin{cases} NH_2 \\ NH_2 \end{cases}$ and *uric acid* $(C_5H_5N_4O_3)$, together with varying quantities of other similar substances, fatty acids in combination with alkalies, the chlorides, sulphates, and phosphates of calcium and magnesium, &c. Fresh normal urine has a slight acid reaction, owing to the presence of monosodium hydrogen phosphate. By putrefaction or fermentation the urea is converted into ammonium carbonate, ammonia being slowly evolved, as is evident from the smell of putrid urine.

$$CO \begin{cases} NH_2 \\ NH_2 \end{cases} + 2H_2O = CO \begin{cases} ONH_4 \\ ONH_4 \end{cases}$$
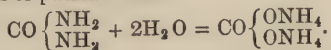
[*] *Journ. Soc. Dyers and Col.,* 1890, p. 39.

The action of urine in washing wool is chiefly due to this ammonium carbonate, which has a mild alkaline character. However, the fatty and albuminous substances, together with the small amount of ammonium phosphate found in urine, may exert some influence. At present urine is not used to such a large extent as formerly, because substitutes have been found which are more regular in composition and pleasanter to work with, especially ammonia and ammonium carbonate. The human urine only is used. It is employed in wool washing, in the manufacture of orchil and cudbear, in the preparation of indigo-vats, and as a fixing agent for aluminium mordants.

Urine substitutes usually consist of crystals of sodium carbonate in a fine state of division. The product which appears in the market in the form of loose lumps contains more or less sodium sulphate and chloride, and often a little soap. The following analyses by Laycock serve to show their general composition :—

	A.	B.	C.
Sodium carbonate, .	23·93	33·93	31·95
,,　　sulphate, .	16·26	3·34	4·04
,,　　chloride, .	0·37	0·25	0·20
Fatty acid, .	1·81	3·32	3·75
Insoluble ash, .	0·22	0·01	0·09
Water by difference,	57·41	59·10	59·97
	100·00	100·00	100·00

URSOL D, P (Ber.). *Oxidation product of paraphenylene diamine.* 1888. Black lumps, insoluble in cold, easily soluble in hot water to a brown solution ; alcoholic solution, brown. Concentrated H_2SO_4, no action, brown tinge only ; on slight dilution, colour quickly dissolves to a bluish-brown solution.

Application.—Brown and black colours are produced on the fibre by the oxidising action of hydrogen peroxide or bichromate of potash. Used in dyeing *hair, fur,* and *wool* on the skin.

USÈBE'S GREEN *v.* ALDEHYDE GREEN.

USNIC ACID *v.* ORCHIL (CHEMISTRY OF).

V

VACANCIN BLUE (H.). A basic dye Gives dark blue on tannin-mordanted cotton.

VACANCIN SCARLET (H.). An azo red produced on the fibre. *v.* AZO DYES.

VALONIA. Like gall nuts and knoppern, valonia is an oak product, being the acorn cups of *Quercus œgilops,* &c. They are larger than

the cups from the ordinary English oak, being from 1 to 1½ inches in diameter. In colour they are drab, and contain 25 to 35 per cent. tannin, but are little used in dyeing.

VALPARAISO WEED *v.* ORCHIL.

VALUATION OF COAL-TAR COLOURS *v.* COAL-TAR COLOURS.

VANADATE OF AMMONIUM *v.* AMMONIUM METAVANADATE.

VANDUARA SILK *v.* SILK (ARTIFICIAL).

VAT RED PASTE (H.). An acid dye, intended to replace barwood as a bottom colour for indigo vat blue.

VEGETABLE PARCHMENT *v.* COTTON (ACTION OF ACIDS ON CELLULOSE).

VENETIAN LAKE *v.* REDWOODS (SOLUBLE).

VENTILAGO MADRASPATANA. This, a native Indian dye of some importance, is known under the various names of "*ouralpatti,*" "*pitti,*" and "*lokandi.*" It is a large climbing shrub belonging to Rhamnaceæ. According to A. G. Perkin* it contains a new colouring matter, which dyes in conjunction with mordants, yielding shades similar to, but bluer than, those produced by camwood.

VERDIGRIS *v.* COPPER ACETATES.

VESUVINE (M.) (B.) *v.* BISMARCK BROWN.

VESUVINE B (B.). *Manchester brown E E* (C.) (Lev.), *Manchester brown P S* (C.), *Bismarck brown T* (D. & H.). An azo dye.

$$
\begin{array}{c}
\textit{Metatoluylene} \\
\textit{diamine}
\end{array}
\left\langle
\begin{array}{l}
\textit{Metatoluylene diamine.} \\
\textit{Metatoluylene diamine.}
\end{array}
\right.
$$

1878. Dark brown powder. Aqueous and alcoholic solution, reddish-brown. Concentrated H_2SO_4, dark brown solution on dilution.

Application.—*v.* BISMARCK BROWN.

VICTORIA BLACK B (By.). An azo dye.

$$
\begin{array}{c}
\textit{Sulphanilic acid azo} \\
\textit{a-naphthylamine}
\end{array}
-
\begin{array}{c}
\textit{Dioxynaphthaline} \\
\textit{sulphonic acid S.}
\end{array}
$$

1889. Black powders. Aqueous solution, dark red-violet. Concentrated H_2SO_4, moss-green solution; on dilution becomes greenish-blue, then bluish-red.

Application.—An acid dye. Dyes *wool* black.

VICTORIA BLACK G, 3 G, and **VICTORIA BLUE BLACK** are similar colours.

VICTORIA BLUE B (B.) (S. C. I.). A diphenylnaphthyl carbinol derivative. *Hydrochloride of phenyl tetramethyl triamido alpha-naphthyldiphenyl carbinol.* 1883. Brown-bronzy crystalline powder. Soluble in water or alcohol with a reddish-blue colour. Concentrated H_2SO_4, yellow; on dilution, yellow, then green, and finally blue.

Application.—A basic dye. Dyes tannin-mordanted cotton blue. Dye *wool* and *silk* best from an acid bath.

* "The Colouring Principles of Ventilago Madras-patana," *Trans. Chem. Soc.,* 1894, p. 923.

VICTORIA BLUE B S (B.) (S.C.I.). Insoluble in water, soluble in alcohol. H_2SO_4 reactions as above.

VICTORIA BLUE R (B.) (S.C.I.). *New Victoria blue* (By.). *Hydrochloride of ethyl tetramethyl triamido alpha-naphthyldiphenyl carbinol.* 1892. Blue powder, soluble in hot water or alcohol with a blue colour. Concentrated H_2SO_4, brownish-yellow solution; on dilution becomes green.

Application.—As VICTORIA BLUE B.

VICTORIA BLUE 4 R (B.) (S. C. I.). *Hydrochloride of phenylpentamethyl triamido alpha-naphthlydiphenyl carbinol.* 1883. Bronzy glistening powder, soluble in water or alcohol with a bluish-red colour. Concentrated H_2SO_4, yellowish-brown colour; on dilution green, then blue.

Application.—As VICTORIA BLUE B.

VICTORIA GREEN 3 B (B.). *New fast green 2 B, 3 B* (S. C. I.). A triphenylmethane derivative. *Hydrochloride or zinc double salt of tetramethyldiamido-dichlor triphenyl carbinol.* 1883. Metallic green crystalline powder. Soluble in hot water or alcohol with a greenish-blue colour. Concentrated H_2SO_4, yellow solution; on dilution, reddish-yellow, then yellowish-green.

Application.—A basic colour. Dyes *wool* or tannin-mordanted *cotton* bluish-green.

VICTORIA ORANGE. An obsolete nitro acid dye.

VICTORIA RED. *Benzopurpurin 4 B* has been sold under this name.

VICTORIA RUBINE (M.) *v.* FAST RED D.

VICTORIA RUBINE O (M.). An acid red dye.

VICTORIA VIOLET 4 B S (M.). A reduction product of chromotrope. 1891. Greyish-green powder. Aqueous solution, dark violet; alcoholic solution, blue-violet. Concentrated H_2SO_4, bluish-red solution; on dilution, yellowish-red precipitate.

Application.—An acid dye producing blue-violet shades on *wool*.

VICTORIA VIOLET 8 B S (M.). A similar compound.

VICTORIA YELLOW. *English yellow, Aniline orange, Saffron substitute.* A nitro compound. *Potassium or ammonium salts of dinitro o-cresol and dinitro p-cresol.* 1869. Reddish-yellow powder, soluble in water with an orange-yellow colour. Concentrated H_2SO_4, light yellow solution.

Application.—Used for colouring butter, margarine, liqueurs, &c.

VICTORIA YELLOW O EXTRA, concentrated (M.) *v.* METANIL YELLOW.

VINASSE *v.* POTASSIUM CARBONATE (COMMERCIAL PREPARATION).

VINEGAR *v.* ACETIC ACID.

VIOLAMINE B (M.) *v.* FAST ACID VIOLET B (M.). Similar to VIOLAMINE G.

VIOLAMINE G (M.). *Acid rosamine A* (M.). Allied to the eosins. *Sodium salt of dimethyl m-amido phenolphthaleïn sulphonic acid.* 1891. Bright red powder. Aqueous solution, yellowish-red; slightly soluble in alcohol. Concentrated H_2SO_4, brownish-yellow solution; on dilution, red-brown solution, then red precipitate.

Application.—An acid colour, dyeing *wool* and *silk* red.

VIOLAMINE R (M.) *v.* FAST ACID VIOLET A, 2 R.

VIOLAMINE 2 R (M.) *v.* FAST ACID VIOLET R.

VIOLANILINE *v.* INDULINE.

VIOLEINE *v.* ROSOLAN.

VIOLET 5 B (By.) *v* METHYL VIOLET 6 B.

VIOLET 6 B (Ber.) *v.* METHYL VIOLET 6 B.

VIOLET C (P.) *v.* CRYSTAL VIOLET.

VIOLET R, 2 R (Mo.) *v.* HOFMANN'S VIOLET.

VIOLET 4 R N (S.C.I.) *v.* HOFMANN'S VIOLET.

VIOLET 5 R (By.) *v.* HOFMANN'S VIOLET.

VIOLET BLACK (B). An azo dye.

$$Paraphenylene\ diamine \begin{cases} \alpha\text{-}naphthylamine. \\ \alpha\text{-}naphthol\ sulphonic \\ \qquad acid\ N\ W. \end{cases}$$

1887. Bronzy glistening powder, soluble in water with a brownish-red colour. Concentrated H_2SO_4, blue solution; on dilution, violet precipitate.

Application.—A direct cotton dye. Dyes unmordanted *cotton* or *wool* violet-black.

VIRGINIA CREEPER (*Ampelopsis hederacea*) contains a red dye which has not been investigated.

VIRIDINE. An obsolete basic green.

VISCOSE *v.* COTTON (CELLULOSE THIOCARBONATE).

VISCOSE SILK *v.* SILK (ARTIFICIAL).

VISCOSITY *v.* LUBRICATING OILS (ANALYSIS OF).

VISCOMETER *v.* VISCOSITY.

VULCANITE *v.* COTTON (ACTION OF NITRIC ACID ON CELLULOSE).

W

WATER. The quality of water used for washing, scouring, bleaching, and dyeing purposes is a matter of the greatest importance, the use of unsuitable water in such operations frequently resulting in faulty work. Goods are often damaged to a greater or less extent from no other cause, and yet, in many instances, because the water happens to be bright and clear, it is not suspected of causing the mischief.

Pure water is a transparent, tasteless, inodorous liquid; colourless when seen in thin layers, but in deep masses it varies from a pale greenish-blue to a deep blue tint. Under ordinary barometric pressure, water boils at the sea-level at 100° C. and freezes at 0° C. According to the thermometer which is commonly used in England (Fahrenheit's) the boiling point of water is 212° and the freezing point 32°. Since the boiling point of a liquid is dependent upon the pressure exerted upon its surface, the temperature of the water in a steam boiler is higher than 100° C. in proportion to the pressure of steam therein. With a pressure of 50 lbs. per square inch, for example, the temperature of the water is 138° C.

Water containing matter in solution boils under the ordinary pressure at a higher temperature than pure water. A saturated solution of common salt boils at 109° C., whilst a saturated solution of calcium chloride boils at 180° C. The amount of added matter present in solutions used in dyeing operations is, as a rule, too small to have any practical effect upon the boiling point of the solution. Where dye-vessels are heated by open steam pipes, the liquid may appear to be in violent ebulition and still have a temperature of several degrees below 100° C.

Water, when heated from 0° to 4° C., contracts in volume, thus forming a striking exception to the almost universal law that bodies expand on heating and contract on cooling. When heated above 4° C. water gradually expands in volume until it reaches 100° C. when it passes off as steam. At 4° C., therefore, water attains its maximum density. In other words, a given volume of water at 4° C. weighs more than at any other temperature. 10,000 volumes of water measured at 4° C. become rather more than 10,001 volumes at 0° C., and about 10,440 at 100° C. When water freezes it undergoes a sudden expansion, equal to about one-tenth of its volume. The force thus exerted is very great, the bursting of water pipes by frost being due to this cause.

Water is 815 times heavier than air. One gallon of pure water weighs exactly 10 lbs. or 70,000 grains. The solvent properties of water are very great—greater, in fact, than those of any other liquid. Its solvent powers vary; some substances dissolve in mere traces, while in other cases a greater weight of solid matter is present than solvent. As a rule, the solubility of a substance increases with increase of temperature. The exceptions, comparatively speaking, are very few, calcium hydrate and sulphate being, perhaps, the most familiar examples. Other salts, alum for example, are exceedingly soluble in boiling water, and only slightly soluble in the cold. Others again, such as common salt, are almost equally soluble in hot and in cold water.

The following table shows the solubility of

rome familiar substances in cold and boiling water :—

	Cold.	Boiling.
Calcium carbonate, . .	·035	..
,, hydrate, . .	1·28	·79
,, sulphate, . .	2·3	2·1
Potassium bitartrate, . .	4	105
Ferrous sulphate cryst., .	36	320
Potassium bichromate, .	100	1,020
,, sulphate, .	100	260
Sodium sulphate (anhy.), .	150	425
,, carbonate (,,), .	160	490
Potassium chloride, .	350	600
Copper sulphate cryst., .	330	1,180
Sodium chloride, . .	360	404
,, hydrate, . .	600	..
Potassium carbonate, .	900	2,050
Sodium bichromate, .	1,000	2,100
Potassium hydrate, .	2,000	..
Calcium chloride, . .	2,000	..
Stannous chloride, . .	2,700	..

Water also possesses the property of dissolving gases. The colder the water the greater the volume of gas dissolved.

The following table shows the solubility by volume of some gases in water at the ordinary temperature, 15° C. :—

Nitrogen, ...	14·8
Hydrogen, ...	19
Oxygen, ...	29
Carbon dioxide, ...	1,002
Sulphuretted hydrogen, . .	3,233
Sulphur dioxide, . . .	43,504
Hydrochloric acid, . . .	462,000
Ammonia, ...	727,200

On account of their remarkable solvent power, all natural waters contain more or less gaseous and solid matter in solution, the nature and amount of the impurity varying greatly according to the nature of the strata with which the water has been in contact. For technical purposes natural waters may be conveniently classified into—(1) Rain water, (2) spring and well water, (3) river and surface water.

Rain water is the purest form of natural water, but during its passage through the air it absorbs various impurities. Rain is water naturally distilled from terrestrial supplies. That which falls in the country is purer than that of towns. It nevertheless invariably contains traces of carbonic, nitric, and nitrous acids ; ammonia, oxygen, and nitrogen, and sometimes traces of saline matter, as well as of finely-divided organic matter. The rain water of large towns usually contains comparatively large quantities of sulphuric acid, derived from the combustion of coal, in addition to small quantities of numerous other substances evolved from various manufacturing processes. After a long spell of mild dry weather the first shower of rain in such places is unusually rich in impurities. Rain water as actually collected, however, often contains many more impurities than those derived from the atmosphere, these varying according to the nature of the surface upon which it has fallen. A slate roof gives the purest water. If collected upon lead or galvanised iron roofs, small quantities of lead or zinc may frequently be detected. In many works, where only hard water is available, it would frequently be found advantageous to pay some attention to the collection and storage of rain water, especially for scouring operations. One inch of rain per acre is equivalent to rather more than 100 tons, or 22,400 gallons, of water. An annual rainfall of 35 inches is thus equivalent on an average to about 2500 gallons of good soft water per acre per working day.

Spring and Well Water.—Of the water which falls as rain a portion evaporates, another portion drains off into brooks and rivers, and the rest penetrates the soil to a greater or less depth according to the nature of the strata. In some cases, after passing through a few yards of permeable strata, such as gravel, sand, or limestone, a less pervious stratum, such as clay, is reached, upon which the water takes an underground course until the stratum crops out at the surface at a lower level. If a well be sunk along the course the water obtained therefrom is known as a shallow well water. On account of the comparative ease with which such water becomes contaminated by sewage and drainage from cultivated land, farm buildings, &c., it does not, as a rule, form desirable drinking water, although it may be very good water for dyeing and other purposes. In some cases the permeable strata do not crop out at the surface but dip down under others which are impervious or nearly so, when the water passes down to a great depth and does not reappear at the surface unless it meets with a fissure and is forced upwards, forming a spring ; the overlying strata may also be bored through so as to form an artificial spring or artesian well.

Spring water and well water usually contain considerable quantities of mineral matter derived from the rocks through which they have percolated. The salts most frequently found in such waters are carbonates, sulphates, chlorides, nitrates, and silicates of calcium, magnesium, sodium, potassium, aluminium, and iron. Calcium and magnesium salts give to water the quality of "hardness," a term signifying the property which such waters

possess of forming insoluble compounds with soaps.

Calcium and magnesium sulphates are soluble in pure water, but the carbonates (except in very small proportions) are only soluble in water containing carbonic acid. The rain as it falls contains a small quantity of carbonic acid ; it acquires a further quantity from decaying vegetable matters in the soil, but a much greater amount from subterranean sources. When water is so highly charged with saline matter that it is unfit for either domestic or technical purposes it is commonly termed a mineral water, of which there are numerous kinds.

River water is composed of a mixture of rain, surface water, and spring water. It also frequently contains more or less drainage water from towns and villages, as well as numerous impurities from various works and factories. River water contains, as a rule, much less dissolved matter than spring and well water, due principally to the admixture of surface water, which often contains very little matter in solution. A portion of the soluble matter in spring water is sometimes gradually deposited, owing to the liberation of carbon dioxide. Carbonates of calcium and magnesium and oxide of iron are thus frequently deposited in the beds of streams and rivers. Surface water from moorland districts is usually of a yellowish-brown or brown colour, due to the presence of peaty acids in solution and other forms of vegetable matter in suspension. River water usually contains a considerable quantity of suspended matter. The Thames contains from 15 to 30 grains per gallon, the Mississippi 56 grains, and the Ganges from 15 to 150 grains per gallon. In this way immense quantities of solid matter are carried into the sea. The Amazon contains only 2 grains of suspended matter per gallon, yet it discharges about 980,000,000 tons of mud into the sea every year.

Character of Impurities.

The impurities in water may be of two kinds, viz.—those which are merely suspended in the water, and those in a state of solution.

Water containing suspended impurities will, of course, appear more or less turbid, while, if dissolved impurities only are present, it will be quite clear and probably colourless. Suspended impurities are thus visible to the eye, and may be got rid of by mechanical means, whereas dissolved impurities can only be detected by chemical reactions and require chemical treatment for their removal.

Mechanical Impurities. — These consist principally of mineral matter in the form of mud and sand, organic matter from the banks of the stream or the gathering ground, and solid matter turned into the river by works or towns situated higher up the stream. The composition and amount of these impurities is very variable, not only in different places, but also at any given place at different times. Generally speaking, however, they do not cause much trouble to the dyer unless present in large amount, although, if oxide of iron is found, the water cannot be considered fit for use in dyeing and scouring operations until the iron has been removed.

All suspended impurities may be got rid of by means of settling tanks or reservoirs, or by filtration. In works where sufficient ground space is available, a very good arrangement is as follows :—The water is pumped from the river into large shallow reservoirs placed at a sufficient height, which it slowly traverses, depositing most of the solid matter during its passage. It then passes down a slight incline, so formed that the water runs in a shallow, broken stream ; the consequent aeration being of special value when an iron salt is present, since the iron is oxidised to ferric oxide, which readily deposits. From the incline the water may be run into storage reservoirs, and thence by gravitation into the works.

It frequently occurs that from want of space or other cause it is impracticable to carry out this system, in which case a simpler but less effectual plan may be adopted, viz. :— The water is pumped into large tanks or cisterns placed on the roof of the works, running from these through fine cloth filters into the water mains.

Dissolved Impurities.—These are much more important from the dyer's point of view than the suspended matters ; and since by far the greater portion of the earth's crust consists of salts of lime and magnesium, these are the chief impurities found in solution ; in fact, natural waters, almost without exception, contain more or less calcium or magnesium compounds. Other substances also are frequently found, and for technical purposes the dissolved impurities may be classified as follows :—

1. Lime and magnesium salts.
2. Compounds of iron.
3. Alkaline impurities.
4. Free acid and acid salts.

1. *Lime and Magnesium Salts.*—These are generally present, either as carbonates (held in solution by free carbonic acid) or as sulphates or chlorides ; and since, in dyeing operations, the action of carbonates differs greatly from that of the last-named salts, every dyer should be able to make such simple tests as are necessary to determine the character and approximate amount of these impurities present.

Detection of Impurities.—*Lime salts* may be detected by adding to a small portion of the water in a test tube a solution of ammonium oxalate, a white precipitate indicating the presence of calcium.

Magnesium salts are not precipitated under these conditions, but on evaporating the liquid to a small bulk after removing the lime salts, an addition of ammonia and ammonium phosphate gives a white precipitate in presence of magnesium.

In order to determine in what form the calcium and magnesium are present, proceed as follows :—

Carbonates of these metals may be detected in two ways :—

(1) A solution of clear limewater gives a white precipitate.

(2) On boiling the water the carbonates are precipitated.

Both these reactions depend upon the fact that calcium and magnesium carbonates are insoluble in pure water, but are dissolved in water containing free carbonic acid, which is present in almost all natural waters. If the free carbonic acid is removed the carbonates thereby held in solution are precipitated, and this is effected by either of the reactions above described, in accordance with the following equations :—

<center>(1)</center>

$$CaCO : H_2CO_3 + Ca(OH)_2 = 2CaCO_3 + 2H_2O.$$
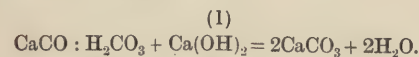
Carbonate of   Lime water.
lime dissolved in
carbonic acid.   (2)

$$CaCO : H_2CO_3 = CaCO_3 + H_2O + CO_2.$$

In the first case the calcium hydrate which is added combines with the carbonic acid which is acting as a solvent, being converted into carbonate of lime, which is precipitated along with that which was originally present in the water.

In the second reaction the carbonic acid is gradually driven off during the boiling, and the carbonate is thus precipitated.

In the case of most samples of water, the lime and magnesium are not present entirely in the form of carbonate, but partly in combination with sulphuric, hydrochloric, or nitric acids. These salts also may be detected in a simple manner. The presence of *chlorides* is indicated, if a white precipitate is obtained by adding a few drops of nitric acid and silver nitrate to the water, while *sulphates* produce a white precipitate of barium sulphate on addition of hydrochloric acid and barium chloride.

Nitrates are less frequently met with, and, if present, contamination with sewage is probable ; and although this may not be of much importance as regards dyeing operations, it, of course, renders the water quite unfit for domestic use. For the detection of *nitrates* a quantity of the water must be evaporated to a small bulk, a little ferrous sulphate solution added, and then concentrated sulphuric acid carefully poured down the side of the test tube to form a separate lower layer of liquid. Nitrates are indicated by the presence of a brown ring at the junction of the two layers.

Determination of Amount of Lime and Magnesium Salts. — The method usually adopted for the estimation of lime salts in water is based upon a fact of every-day experience—viz., that hard water will not form a lather with soap until a certain amount of the soap has been employed.

At first the soap produces a mere curdy scum or precipitate, but by continuing the rubbing a lather is eventually obtained. The explanation of this fact is as follows :— Ordinary soap consists of fatty acids, say oleic, stearic, or palmitic acid, in combination with either sodium or potassium. These salts of fatty acids or soaps are, however, decomposed by salts of other metals, such as calcium, magnesium, iron, &c., the resulting compounds or soaps being insoluble in water, and of a sticky or curdy nature.

The scum produced when soap is employed in conjunction with "hard" water consists, indeed, of the insoluble lime soap, and until the whole of the lime, &c., present in the water is thus combined, no lather is produced.

The amount of soap destroyed by a given quantity of the water before the lather is produced, may thus serve as a measure of the lime, &c., present in the water ; although, for reasons which will be touched upon later, the determination is by no means an accurate one.

Temporary and Permanent Hardness.—On boiling a water containing carbonate of lime in solution, the carbonic acid, which holds the carbonate in solution, is driven off, and the latter is precipitated. If the water is then filtered, the lime originally present as carbonate is entirely got rid of. On this account, a water containing carbonates only, is said to possess "removable" or "temporary" hardness ; while a water in which sulphates or chlorides are present is said to be "permanently" hard, because the hardness is not removed by boiling. Most samples of water possess both "temporary" and "permanent" hardness, the sum of the two giving the "total" hardness.

In making an estimation of the hardness of water by means of soap, the "total" hardness is first determined, and then another portion of the water is boiled and filtered (thus removing the carbonates) and the "permanent" hardness estimated, the difference between the two giving the "temporary" hardness which was lost during the boiling.

The soap test for hardness was devised by Clark, and is commonly known by his name. The process is still used to some extent as originally introduced, and is so arranged that 1° of hardness is equivalent to 1 part $CaCO_3$ per 100,000 parts water; the lime and magnesium salts, whatever their character, being expressed in terms of $CaCO_3$.

Of the various methods which have been proposed for carrying out the soap test, that of Wanklyn is perhaps the simplest. In this the degrees of hardness represent grains $CaCO_3$ per 70,000, and this scale is also adopted by Frankland.

The soap solution is prepared by dissolving 10 grms. of pure castile soap in 600 c.c. of alcohol, and diluting to 1 litre with distilled water. The solution is standardised by means of an artificial hard water, prepared by dissolving 1·11 grm. of pure anhydrous calcium chloride in 1 litre water. This is most readily done by weighing exactly 1 grm. pure $CaCO_3$, dissolving in a slight excess of hydrochloric acid, then evaporating to dryness, to remove excess of acid, which is ensured by adding a little water, and again evaporating to dryness. Finally, the calcium chloride thus produced is dissolved in 1 litre of water.

Standardising the Soap Solution.—10 c.c. of the calcium chloride solution are introduced into a 10-oz. stoppered bottle, and diluted with 60 c.c. of distilled water. The soap solution is added in small quantities (about 1 c.c.) at a time from a burette, and the bottle well shaken. When the lather begins to disappear somewhat slowly, smaller quantities are added at a time, and the bottle, after shaking, is placed on its side. The operation is complete when an unbroken lather remains permanent for five minutes. If the soap solution is of the correct strength 11 c.c. will have been required to produce this effect, and if too strong, the soap solution must be diluted until it is of the requisite strength. The reason 11 c.c. is required for 10 c.c. of the calcium chloride solution is that 1 c.c. of soap solution is used up in producing a lather with 70 c.c. of pure water.

The 70 c.c. of calcium chloride solution (= 10 c.c. of the standard solution) contain the equivalent of ·001 grm. $CaCO_3$—that is, 1 part in 70,000. Each 1 c.c. of soap is thus equal to 1 part $CaCO_3$ per 70,000, or 1 grain per gallon.

Estimation of Total Hardness.—70 c.c. of the water are titrated with the standard soap solution until a permanent lather is produced, and the number of c.c. required, less 1 c.c., gives the degrees of hardness.

Estimation of Permanent Hardness.—70 c.c. of the water are boiled for thirty minutes with reflex condenser, then cooled, diluted to 70 c.c. with distilled water, filtered, and the hardness determined as before.

Estimation of Temporary Hardness.—The difference between permanent and total hardness gives the temporary hardness—*i.e.*, the hardness due to the precipitated carbonates. It should not be forgotten, however, that calcium carbonate is soluble in pure water to the extent of 2 grains per gallon, and that the soap test therefore always shows a deficiency of about 2° in temporary hardness, and an excess of the same amount in permanent hardness over the amounts of carbonate and sulphate really present in the water.

This soap test for hardness, although very useful, cannot by any means be considered an accurate analytical process for the estimation of the lime and magnesium salts, since the results obtained are influenced by the presence of many other substances. For instance, the presence of free acid or alkali gives a reading correspondingly too high or too low; the former increasing and the latter decreasing the apparent hardness, as indicated by the soap test. To take an extreme case. If carbonic acid gas is led into pure distilled water, the latter may show 10° or 12° of hardness by the soap test, although, of course, no lime whatever is present.

Again, in the case of samples of water that possess more than about 15° of hardness the test is very unreliable. A sample may, for instance, show 25° of hardness if 50 c.c. is titrated in the usual way, but if 25 c.c. is taken, diluted with 25 c.c. of pure water, and then titrated, the number found, on multiplying the result by two, may be 35°, or even 40° hardness. It is evident, however, that for practical purposes the supposed sample is only 25° hard as regards soap-destroying power, since in practice it would not be diluted. In other ways also the relative proportion between soap-destroying power and the actual amount of Ca and Mg present varies in an erratic and unexplained manner.

The acidimetric test is a much more accurate method of determining the actual amount of lime, &c., present as carbonate and as sulphate. In this process the temporary hardness is estimated directly by titrating a known volume of the water with standard $\frac{N}{100}$ acid, using methyl orange or lacmoid as an indicator. If any free alkali is present the result will, of course, be too high; but free carbonic acid does not influence the result. The total hardness is determined by evaporating a known volume of the water to dryness in the presence of carbonate of soda, which changes the sulphates of lime, &c., into carbonates. The precipitated carbonate is then collected on a filter, washed free from excess of soda, dis-

solved in a known amount of standard acid, and the excess of the latter determined by titration with standard alkali. The amount of acid necessary to neutralise the whole of the lime, &c., present in the water is thus arrived at, and if the temporary hardness is deducted from this, the permanent hardness, due to sulphates, &c., is obtained.

Iron as an Impurity.—Iron is frequently present in water which is obtained from beds of shale, or from iron or coal mines ; and from a dyer's point of view is an even more objectionable impurity than calcium and magnesium. When iron is present in considerable amount the water is termed a chalybeate water. Examples of such are found at Spa, Tunbridge Wells, and in one of the Harrogate springs, but waters of this type are not employed industrially.

The presence of iron in smaller quantities is, however, frequently demonstrated by the appearance of brown ferric oxide on half-covered stones in a river or stream.

Iron is usually present in water, either as carbonate, held in solution by free carbonic acid, or as sulphate. The latter is produced by the atmospheric oxidation of naturally occurring ferrous sulphide (iron pyrites). The ferrous sulphate thus produced readily undergoes further oxidation, and finally dissociates, ferric oxide being precipitated and sulphuric acid remaining in solution. On account of this decomposition, a water which contains iron, or from which the iron has been precipitated, also frequently contains free sulphuric acid.

Detection of Iron.—The presence of any considerable amount of iron is usually rendered self-evident by the formation of the brown deposit of ferric hydrate before referred to, but definite information as to the presence or absence of iron is obtained by applying the following test :—A quantity of the water (say 200 c.c.) is made slightly alkaline with carbonate of soda, and then evaporated to small bulk. If a deposit is obtained it should be collected on a filter, washed, and dissolved in a small amount of pure hydrochloric acid. The acid solution is then boiled with a few crystals of potassium chlorate, to oxidise any ferrous into ferric salt. A few drops of potassium ferrocyanide (yellow prussiate of potash) solution is added, which at once produces a blue precipitate if iron was present in the original water.

A simpler, but less conclusive, test is to add to a sample of the water a few drops of a freshly made decoction of logwood (not logwood extract). In pure water a straw colour only is given, whereas the presence of even a trace of iron results in the development of a grey or black colour. Lime or magnesium salts produce a claret or purple coloration. A solution of tannic acid (from gall-nuts,

sumach, or myrabolans) also furnishes a delicate test for the presence of iron (ferric) salts, extremely dilute solutions of the latter, giving a blue or black coloration.

Free Acids as Impurities.—The source of free sulphuric acid as a water impurity has already been alluded to.

Ferrous sulphide is oxidised to ferrous sulphate, which being dissolved by the water is gradually decomposed, ferric oxide being deposited and sulphuric acid liberated ; and in the absence of carbonates the free acid remains in the water. Sulphuric acid is the only mineral acid which is at all commonly met with, but certain organic acids, derived from decomposing vegetable matter, are of frequent occurrence in surface water; these so-called peaty acids being an objectionable impurity on account of their solvent power for iron and lead.

Free carbonic acid is also generally present in water, but since it is expelled on boiling it does not cause any trouble during dyeing processes, although it will decompose a certain amount of soap in scouring operations. The presence of peaty acids imparts a yellow or brownish colour to the water, and in the absence of other oxidisable impurities the amount may be approximately estimated by noting the amount of a standard solution of potassium permanganate destroyed by a given volume of the water. Sulphuric acid may be estimated by titrating with $\left(\frac{N}{100}\right)$ alkali, using methyl orange as indicator.

Alkaline Impurities.—Water from wells which tap the lower coal measures not unfrequently contains sodium carbonate in considerable amount, as much as 20 parts Na_2CO_3 in 100,000 parts water (= 2 lbs. per 1000 gallons) being by no means rare. Any such quantity as this would, of course, exert a great effect in many dyeing operations, but, fortunately, its action can be neutralised by adding the corresponding amount of sulphuric acid. The presence of free alkali may be detected by means of a suitable indicator, such as red litmus paper, phenolphthaleïn, &c.

Lead and Copper Impurities.—Salts of these metals are of much less frequent occurrence than calcium, magnesium, or iron compounds, although if present they are equally objectionable. Lead may be detected by evaporating 1 litre of water to about 50 c.c. ; adding a few drops of acetic acid and then passing sulphuretted hydrogen gas through the solution ; a brown coloration being obtained if lead is present. If a little potassium ferrocyanide is added to the concentrated water, a brownish-red coloration indicates that copper is present.

Water for Boiler Purposes.—In a steam boiler, since practically pure water comes off as steam, the solid matter in solution

gradually accumulates; and, in most cases, a portion of it, sooner or later, is deposited. If the deposit is of a loose, powdery character, it forms what is known as "boiler mud;" if it becomes firmly attached to the boiler plates it is known as a boiler "incrustation." Waters which form a hard incrustation are either to be avoided for boiler purposes, or they should be treated in such a manner as to prevent its formation. Incrustations not only cause much loss of heat, but the boiler plates are liable to be damaged through over-heating. An incrustation is usually associated with a "hard" water, and there are many large users of steam who consider that incrustations are formed in proportion to the hardness of the water used. This is a mistake, since much depends upon the character of the salts constituting the hardness. A com-paratively soft water may produce a hard scale much more quickly than a very hard one. If, for example, the hardness of a water was due entirely to either calcium chloride or magnesium sulphate (which is seldom the case, however), no incrustations would be formed under ordinary conditions, since both are very soluble salts. If the hardness of the water used is entirely due to bicarbonates the excess of carbonic acid is quickly given off in the boiler, and normal carbonates of lime and magnesia are precipitated, not on the boiler plates, but as a loose powdery mass. If the hardness is due entirely to sulphate of lime, no precipitation takes place until the water becomes very much con-centrated—until it contains about 150 grains of calcium sulphate per gallon. At this stage the water is saturated, and further concentration causes the calcium sulphate to crystallise on the boiler plates in the form of a hard deposit. When calcium and magnesium carbonates are present as well, these salts also become incorporated with the calcium sulphate. Water containing magnesium bicarbonate, deposits at first magnesium carbonate; but Driffield,* in a valuable paper on "Boiler Management," has shown that boiler incrustations, though thrown down as a powdery mass, contain the magnesia in the form of hydrate, $Mg(OH)_2$. He further points out that this hydrate of magnesia (even in the absence of calcium sulphate) is liable to bake into a hard scale if the flues are not well cooled down before the boiler is blown off. Calcium carbonate may also bake on to the plates under the same conditions, but not so readily as magnesium hydrate.

In order to prevent the formation of scale in steam boilers many so-called "boiler com-positions" have been proposed and used. Some work satisfactorily, but the majority are altogether useless and, in some cases, positively injurious. A compound may, of

* Journ. Soc. Chem. Ind., xi., p. 178.

course, act beneficially with one kind of water and yet be altogether useless for another. The best way is to remove the scale-forming ingredients before the water enters the boiler. Driffield shows, however, in the paper above mentioned that very satisfactory results may be obtained by merely adding sufficient sodium carbonate to convert the calcium sulphate into calcium carbonate. Water containing magnesium chloride is liable to act injuri-ously upon the boiler plates, from its decom-position into magnesium hydrate with evolu-tion of hydrochloric acid. If magnesium chloride be present, sodium carbonate should therefore also be added in sufficient quantity to convert it into carbonate.

Water for Scouring, Washing, and Bleaching Purposes.—In all these opera-tions salts of lime, magnesia, and iron are very objectionable. Iron is usually present in very much smaller quantities than lime and magnesia, but traces of iron in water are frequently the cause of much trouble. One thousand gallons of water destroy about 1 lb. 7 ozs. of soap for every degree of hard-ness, but this loss of soap is not by any means the only disadvantage. The sticky, insoluble calcium and magnesium soaps which are precipitated, are liable to be deposited irregularly on the goods, and such being the case, uneven dyeing — especially with "mordant" colours — is almost invariably the result. If more than a trace of iron is present in the water, an insoluble iron soap will be precipitated on the fibre, and on being subsequently dyed with any "mordant" colour, the shade will be dull and probably stained. For bleaching purposes, water con-taining iron is very objectionable, whether the goods are to be subsequently dyed or to remain white. Very small quantities of oxide of iron are sufficient to give a yellowish tinge to bleached fabrics, and to dull such shades as Turkey-red. Water highly coloured with organic matter (peaty acids) is unsuit-able for bleaching and stoving purposes. Water obtained from the lower beds of the coal measures often contains large quantities (20 to 40 grains per gallon) of sodium car-bonates. Such water, in the absence of earthy carbonates, acts beneficially in scour-ing operations, and is highly valued by wool combers and manufacturers who use large quantities of soap. Alkaline water is, how-ever, very objectionable in washing off after dyeing.

Water for Mordanting and Dyeing Pur-poses.—The most troublesome waters to the dyer are those containing iron (in any form), and *carbonates* of lime, magnesia, and soda. Sulphates have little or no action in dyeing, but in the subsequent washing operations a considerable amount of earthy sulphates in the water may act injuriously in certain cases

by "saddening" or "bleeding off" the colours. In mordanting operations, the carbonates produce precipitates with salts of iron, aluminium, tin, &c., and reduce bichromates to neutral chromates. The active ingredient is thus rendered much less effective as a mordant. If organic acids or acid salts (such as tartar) are used, a portion is neutralised and thereby rendered useless. Alkaline carbonates act more powerfully in these respects than calcium and magnesium carbonates. In dyeing operations, carbonates modify the colours produced with various dyes—especially cochineal scarlets, which are rendered much bluer than shades dyed in pure water. Many colouring matters, such as methyl violet, Victoria blue, coeruleïn, alizarin blue, &c., are precipitated by carbonates. The dye thus works on to the material in a loose form and in many cases produces stains. It is not thoroughly fixed; and, when rubbed, much of the colour is removed, and stains whatever material it comes in contact with. In some cases, as, for example, in the dyeing of alizarin red (either upon wool or cotton), lime salts are decidedly beneficial when the material has been mordanted with aluminium compounds. The effect of acetate of lime in dyeing with alizarin upon wool has been clearly illustrated by Hummel.* Alkaline carbonates retard the dyeing of most colouring matters; a small quantity of sodium carbonate, for example, is sufficient to prevent logwood dyeing at all. Earthy carbonates in moderate quantity produce deeper though duller shades with logwood, fustic, &c. In dyeing with "acid" colours neither sulphates nor carbonates have practically any effect. The amount of acid used is, as a rule, great, in proportion to the alkalinity of the water, consequently as large quantities of sodium sulphate are generally added at the same time, the comparatively small quantities of calcium, magnesium and sodium sulphates (formed by the action of the sulphuric acid on the carbonates), cannot be expected to appreciably affect the results. In many cases, after the dyeing proper, the colour is seriously injured by washing or showering with water containing a large amount of earthy and alkaline carbonates. Too little importance is often given to the kind of water used in washing dyed goods. The effect of *iron* in water used for dyeing is to "sadden" or dull almost all "mordant" colours. A very small quantity either in the mordant or dye-bath has a most marked effect upon shades produced with such colouring matters as alizarin red, cochineal, &c. The effect is much greater when separate baths are used for mordanting and dyeing than when the single bath method is adopted. In the latter case the bath is usually of an acid character;

* *Journ. Soc. Dyers and Col.*, 1834, p. 11.

and the iron does not readily become fixed on to the fabric. With "acid" dyes the amount of iron usually present in natural waters produces little or no effect.

Lead is seldom present in waters used for dyeing, but its action in wool dyeing has been studied by Rawson,* who finds that bright colours dyed in a neutral bath are very much affected, whereas in the presence of acids the same amount of lead has no action. The "saddening" effect is evidently caused by the sulphur naturally present in the wool combining with the lead to form black sulphide of lead. In the presence of sulphuric acid, however, this combination does not take place.

Correction of Water used in Dyeing.— Methods for the general purification of water are described below, but, in the absence of iron, for most dyeing purposes all that is necessary is to carefully neutralise the earthy and alkaline carbonates which may be present with an acid. This may be done in the mordant or dye-bath with either sulphuric acid or acetic acid. The former acid is much cheaper, but great care must be taken not to use too much, otherwise bad results will be obtained. On this account, on dyeing with alizarin blue, coeruleïn, and other similar colours in calcareous waters, it is much better to use *acetic* acid, since a slight excess does no harm. In mordanting with bichromates, sulphuric acid may be used with advantage for neutralising any carbonates. The amount of sulphuric acid (D.O.V.) required for neutralising 1000 gallons of the water may be readily ascertained in the following manner: —Pour 1 litre of water into a white basin and add a few drops of a solution of methyl orange. Add from a burette, during constant stirring with a glass rod, a solution containing $6\frac{1}{4}$ grms. of sulphuric acid in a litre of distilled water until the colour of the liquid changes to red. The *number of cubic centimetres* thus required corresponds to the *number of ounces* of sulphuric acid to be added to 1000 gallons of the water.

Purification of Water.—The supply of water is frequently of such a quality that it is found desirable to effect some means of purification. On a small scale, for the laboratory, &c., water is best purified by distillation. In many works a considerable amount of distilled or condensed water is obtained from the steam pipes and used for scouring purposes. This practice might be much more widely adopted; the condensed water could not possibly be used to greater advantage. A pure soft water is a greater necessity in scouring than in any other operation. Suspended matter in water is readily removed by filtration through beds of sand and gravel or engine ashes.

* *Journ. Soc. Dyers and Col.*, 1889, p. 53.

Many substances, especially iron, are wholly or partially removed by exposure to air in large shallow dams and subsequent filtration. Waters highly charged with bicarbonates give off a portion of their carbon dioxide, and normal carbonates are precipitated. Excepting in the case of waters containing ferrous carbonate, however, the change takes place very slowly and is never complete. Ferrous carbonate in water is quickly decomposed on exposure to air, and ferric hydrate is thrown down as a reddish-brown precipitate.

For the purification of water by chemical means numerous substances have been proposed. The principal impurities to be removed are bicarbonates and sulphates of lime and magnesia, as well as iron and organic matter. It has been already stated that bicarbonates in water are decomposed and precipitated by boiling. A similar effect is produced by adding calcium or sodium hydrate to the water. When lime is used, the free carbonic acid unites with it to form calcium carbonate, which is precipitated as well as the calcium or magnesium carbonate previously existing in the form of soluble bicarbonates. When caustic soda is used, sodium carbonate is formed, which remains in solution. The following equations illustrate the changes which occur :—

(1) $CaO(CO_2)_2 + CaO = 2CaCO_3$.

(2) $MgO(CO_2)_2 + CaO = MgCO_3 + CaCO_3$.

(3) $CaO(CO_2)_2 + 2NaHO$
$= CaCO_3 + Na_2CO_3 + H_2O$.

(4) $MgO(CO_2)_2 + 2NaHO$
$= MgCO_3 + Na_2CO_3 + H_2O$.

It is very important that the exact amount of precipitant should be added ; otherwise, when *lime* is used, the water may be rendered harder than it previously was, either by a deficiency or an excess. If the water contains free carbonic acid, some of the lime will be converted into bicarbonate and remain in solution. On the other hand, if too much lime is added, the whole of the carbonic acid is removed, but calcium hydrate remains in solution. The treatment with lime or soda also precipitates any iron which may be present in the water, as well as a portion of the organic matter. When much organic matter is present, in order to obtain good results it is necessary to employ some soluble salt of alumina or iron in addition to lime or soda.

The alumina or ferric oxide formed carries down the organic matter and also causes the carbonates of lime and magnesia to settle more rapidly.

Waters containing sulphates of lime and magnesia undergo no change upon boiling (unless highly concentrated), and are not acted upon by calcium hydrate. Sodium hydrates act differently according to whether sulphate of lime or sulphate of magnesia only is present, or whether carbonates are present as well. In the absence of carbonic acid sodium hydrate produces no effect upon water containing calcium sulphate ; but magnesium sulphate is precipitated as hydrate in accordance with the following equation :—

$MgSO_4 + 2NaHO = Mg(HO)_2 + Na_2SO_4$.
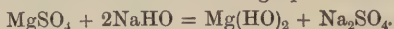
When carbonic acid is present in water, either free or as bicarbonate, on the addition of sodium hydrate, sodium carbonate is formed, which then reacts upon calcium sulphate with the formation of carbonate :—

$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4$.

Unless calcium sulphate is present in excess, the addition of caustic soda thus effects the removal of both carbonates and sulphates of the alkaline earths. The caustic soda is most economically obtained by using a mixture of quicklime and soda ash. If the free carbonic acid present is but small in amount, or the calcium sulphate excessive, an addition of sodium carbonate must be made. Sodium carbonate also precipitates magnesium salts as carbonates ; but the hydrate of magnesia is less soluble than the carbonate, hence caustic soda is the best precipitant. The method of purification by means of lime is commonly attributed to the late Dr. Clark, of Aberdeen, although, according to the late Dr. Angus Smith, the use of lime was first proposed about a century ago by Thomas Henry, of Manchester. In its simplest form, as originally devised, two tanks or reservoirs are employed—one being used for mixing the hard water with the requisite amount of milk of lime or, preferably, clear lime water, and the other to receive the purified water after the insoluble matter has been allowed to subside. A better plan is to have two mixing or precipitating vessels of such a size that each will hold sufficient water for a day's supply. The precipitated calcium and magnesium carbonates settle slowly, and the vessels used should therefore be shallow. On this account a considerable space is required to carry out the process with success. Of late years, however, numerous forms of apparatus have been devised with the object of economising space and time, as also of obtaining a continuous flow of pure soft water.

Complete Quantitative Analysis of Water for Dyeing, Scouring, Steam Raising, and other Technical Purposes.

Grms. per litre × 70 = grains per gallon.

Collection of Samples.—Two clean "Winchester quart" bottles should be rinsed out twice with the water to be tested, and if the sample is to be taken from a well, tank, or

stream, the bottles should be completely immersed and filled up to the neck. Care should be taken to avoid any matter which is not a normal constituent of the water, such as dirt, grease, scum, &c., finding access to the bottle. If the sample be obtained from a tap or pump, the water should be allowed to flow for a few minutes before rinsing out and filling the bottles. The glass stoppers must be inserted immediately and securely tied down with string.

Determination of Suspended Matter.—If on shaking, the sample is found to contain a considerable amount of suspended matter, 1 or 2 litres, according to the apparent amount of insoluble substances present, may be filtered through a filter paper which has been previously dried in the steam-bath until of constant weight. When the water has passed through the filter, it is removed, and this portion, together with the whole of the remaining water (which should be filtered at once through an unweighed filter paper), afterwards used in the subsequent determinations.

The insoluble matter on the weighed filter paper is well washed with cold water, and dried in the water-bath until of constant weight.

The increase in weight of the filter paper = total suspended matter in 1 litre.

The *insoluble mineral matter* may be estimated by igniting the filter paper and its contents in a platinum basin, and heating over a Bunzen flame until a constant weight is obtained.

Non-volatile residue = insoluble mineral matter in 1 litre.

The total insoluble matter *less* the insoluble mineral matter = the suspended organic and volatile matter in 1 litre.

Total Saline Matter.—1 litre of the water is evaporated to dryness in a weighed platinum basin, and the residue dried in the water-bath until no further loss in weight takes place.

Weight of residue = total saline matter (dried at 100° C.) in 1 litre.*

Organic and Volatile Matter.—The residue of total saline matter is very carefully heated over a low flame, and eventually gently ignited until a constant weight is obtained.

Loss in weight on ignition = organic and volatile matter in 1 litre.

Total saline matter *less* organic and volatile matter = soluble mineral matter in 1 litre.

In many instances the weight of the soluble mineral matter thus estimated is a check upon the results of the analysis of the various constituents. In other cases, however, where such salts as calcium nitrate, magnesium carbonate, &c., are present in the water in con-

* It is often advisable to dry again at 150° C., in order to drive off all chemically-combined water.

siderable quantities, the weight of the total saline matter obtained directly is of minor importance.

Silica.—The platinum basin containing the residue from the previous determination is covered with a clock-glass, and an excess of dilute hydrochloric acid added. The under side of the clock-glass is rinsed with distilled water into the dish, and the solution evaporated to dryness. The basin and its contents are then heated in an air-bath at a temperature of about 130° C. for an hour to render the silica insoluble. When cold, strong hydrochloric acid is added in rather more than sufficient quantity to moisten the residue, and after standing about fifteen minutes, boiling water from a wash-bottle is added. The liquid is then poured through a small ash-free filter, the residue well washed, dried, ignited, and weighed.

The residue = grms. silica in 1 litre.

Oxide of Iron and Alumina.—To the filtrate and washings from the silica (the volume of which should not exceed 100 c.c.) are added about 3 drops of strong nitric acid, and the liquid boiled for a few minutes. Ammonium chloride and a slight excess of ammonia are next added, and the beaker is heated on the water-bath until the smell of ammonia has disappeared. The precipitate is then filtered (as small a filter as possible being used), thoroughly washed with hot water, dried, gently ignited, and weighed.

Residue = grms. $Fe_2O_3 + Al_2O_3$ in 1 litre.

Oxide of Iron.—The ignited precipitate of oxides of iron and aluminium is dissolved in a little concentrated hydrochloric acid, and diluted to 100 c.c., and estimated by one of the following methods :—

Estimation of Iron by Colour-titration with Potassium Ferrocyanide.—A dilute standard solution of iron containing 0·00001 grm. of Fe per c.c. is prepared as follows :—

0·7 grm. of pure ferrous ammonium sulphate (= 0·1 grm. Fe) is dissolved in water, acidulated with sulphuric acid, oxidised by the careful addition of a drop of dilute potassium permanganate until the liquid is just pink, when it is diluted to 1 litre. 100 c.c. of this solution are then further diluted to 1 litre. The latter solution is then of the strength mentioned above.

10 to 50 c.c. (according to the apparent quantity of iron present) of the 100 c.c. to be tested, are placed in a Nessler tube, 1 c.c. of strong hydrochloric acid (free from iron), and 1 c.c. of a solution of potassium ferrocyanide are added, the liquid made up with water to the 50 c.c. mark and well stirred.

A quantity of the standard iron solution, judged sufficient to produce the same depth of colour (1 to 5 c.c.), is run into a similar tube, the same quantities of acid and potassium ferrocyanide added, and the liquid made

up to 50 c.c. After allowing five minutes for the colour to develop, the depth of colour in the cylinders is carefully compared, and a fresh experiment made, using more or less of the standard iron solution as may be required until similar depths of colour are obtained.

Example.—The precipitate of oxides of iron and alumina from 1 litre of water was dissolved in acid and diluted to 100 c.c. 10 c.c. of this solution produced the same depth of colour with potassium ferrocyanide as 6 c.c. of the standard iron solution. One litre of the water, therefore, contained $0.00001 \times 6 \times 10 = 0.0006$ grm. of Fe.

Estimation of Iron by Colour-titration with Potassium Thiocyanate.—Exactly the same method of manipulation is adopted as when ferrocyanide is used, but in this case the colour produced is red. The reaction is exceedingly delicate; 1 part of iron can be recognised in fifty million parts of water.

Lime.—The filtrate from the precipitate of oxides of iron and aluminium is made alkaline with ammonia, ammonium chloride (to keep the magnesia in solution) and ammonium oxalate added, the solution well stirred, and the beaker kept in a warm place for a few hours. The liquid is poured through a filter, the precipitate of calcium oxalate thoroughly washed, dried, and gently ignited in a platinum crucible. The calcium oxalate is then completely converted into oxide by strongly heating over the blowpipe until it ceases to lose weight.

Weight of precipitate = grms. CaO in 1 litre.

If the quantity of calcium oxalate after drying exceeds 1 grm. its conversion into oxide is only accomplished by prolonged heating. In that case the calcium oxalate and filter paper should be placed in a weighed platinum basin and gently ignited. By this means the oxalate is converted into carbonate of calcium. When cold, the basin is covered with a clock-glass, dilute sulphuric acid in excess carefully added, and heated, until no further effervescence takes place, on the water-bath. The clock-glass is then rinsed into the basin and the liquid evaporated to dryness, thoroughly dried in the steam-bath, gently heated over a bunsen flame, and ignited until of constant weight.

Residue $(CaSO_4) \times \frac{56}{136}$ = grms. CaO in 1 litre.

Magnesia.—The filtrate and washings from the calcium oxalate precipitate are transferred to a porcelain basin and concentrated by evaporation to about 50 c.c. ;* when cold,

* If a large quantity of ammonium chloride be present, it is advisable to remove it before precipitating the magnesia. The basin is covered with an inverted funnel, which should just fit inside the basin, and for each grm. of ammonium chloride supposed to be

ammonia in excess, and a solution of sodium phosphate added, the mixture well stirred, and allowed to remain undisturbed for twelve hours.

The liquid is decanted from the precipitate of ammonium magnesium phosphate $(MgNH_4P_2O_4)$ on to a filter, and the whole brought on to the filter by means of the filtrate, in order to make the amount of wash water as small as possible. The precipitate is then washed with dilute ammonia (1 part .880 ammonia to 5 parts of water) until a few drops of the filtrate cause merely the faintest turbidity with pure nitric acid and silver nitrate. The filtrate is measured, and for each 50 c.c. of liquid, 0.001 grm. is added to the weight of magnesium pyrophosphate eventually obtained.

The precipitate is dried, detached from the filter paper as completely as possible, and transferred to a porcelain crucible, in which it is very gently heated, at first with the lid on, for fifteen minutes. The temperature is now raised, and after removing the Bunsen flame, the filter ash, which should be completely burnt, is added. The crucible is then strongly ignited for fifteen minutes, cooled, and weighed.

The residue $(Mg_2P_2O_7) \times \frac{40}{111}$ = grms. MgO in 1 litre.

Potash and Soda.—One litre of water is acidulated with hydrochloric acid, and evaporated in a basin to about 150 c.c. A little pure baryta (not above 0.2 grm.) is added, and after heating the mixture for a quarter of an hour, the precipitated magnesia, iron, alumina, sulphates, phosphates, and carbonates are filtered off and well washed. The filtrate is concentrated, ammonium carbonate and ammonium oxalate added to precipitate the calcium and barium. These substances are filtered off, washed, and the filtrate and washings evaporated to dryness in a porcelain basin, thoroughly dried in the water-bath, and the ammonium salts carefully expelled by gentle heating. The residue is treated with a small quantity of water, filtered from any insoluble matter, and the filtrate and washings received in a weighed platinum dish. The solution is acidified with hydrochloric acid and evaporated to dryness. The basin and its contents are heated in the steam-bath and eventually gently ignited, at first over a

present, about 3 grms. of strong nitric acid added. The basin is placed on a water-bath, when effervescence sets in owing to the decomposition of the sal ammoniac. The liquid is heated until the effervescence ceases, when the funnel is rinsed into the basin, and the solution evaporated to dryness. The saline mass in the basin is dissolved in water, a small quantity of ammonium chloride added, and the solution rendered strongly ammoniacal, filtered if necessary, the precipitate (silica, &c.) dissolved from the dish) well washed, and the filtrate treated with sodium phosphate as above.

23

very small flame, until the mixed alkaline chlorides cease to lose weight.

Residue $(KCl + NaCl)$ = grms. mixed alkalies in 1 litre.

The *potassium* may be determined by precipitation as double platinum salt by means of platinum tetrachloride. *v.* POTASSIUM.

Indirect Estimation of Potassium and Sodium by Titration with Silver Nitrate.— The weight of the mixed alkaline chlorides obtained as above is ascertained and noted. The mixed salts are transferred to a porcelain basin and very carefully titrated with $\frac{N}{10}$ $AgNO_3$, using potassium chromate as indicator. *v.* SODIUM CARBONATE (ANALYSIS). The chlorine found is calculated to NaCl.

Wt. of mixed chlorides—Wt. NaCl = x.

$$x \times 2{\cdot}4286 = \text{wt. of K.}$$

Wt. of K × 2 = grm. potassium in 1 litre.

Treatment of Total Saline Matter with Sulphuric Acid.—It is sometimes sufficiently accurate to estimate the sodium (disregarding potassium) indirectly, the total alkali being reckoned as sodium. 500 c.c. of water are treated with an excess of sulphuric acid and evaporated to dryness. All the metals are thus converted into sulphates. The residue is gently ignited with ammonium carbonate, cooled, and weighed.

Residue × 2 = grms. silica + total metals as sulphates in 1 litre.

Sulphuric Acid as Sulphates (and Free Sulphuric Acid if present).—One litre of water is acidified with hydrochloric acid, and evaporated in a beaker over a rose-burner, to about 100 c.c. when a slight excess of barium chloride is added. The barium sulphate is allowed to stand for some hours, filtered, washed, dried, ignited, and weighed. *v.* ACIDIMETRY (STANDARD SULPHURIC ACID).

Wt. $BaSO_4 \times \frac{8 \cdot 0}{2 \cdot 3 \cdot 3}$ = grms. SO_3 in 1 litre.

Free Sulphuric Acid.—250 c.c. of water are placed in a porcelain basin and titrated with $\frac{N}{10}$ or $\frac{N}{100}$ NaOH, using lackmoid as indicator.

1 c.c. $\frac{N}{10}$ NaOH = $0{\cdot}0049$ grm. H_2SO_4. grms. sulphuric acid × 4 = grms. free H_2SO_4 in 1 litre.

Chlorine.—One-half litre of water is titrated in a porcelain basin with $\frac{N}{10}$ silver nitrate and potassium chromate. *v.* SODIUM CARBONATE (ANALYSIS).

Wt. of chlorine × 2 = grms. chlorine per litre.

If the amount of chlorine present be large (as ascertained by a preliminary qualitative test with nitric acid and silver nitrate), 100 c.c. will be a sufficient quantity to take for this determination. On the other hand, if the amount of chlorine be very small, or if only a small amount of the sample be to

tested be available, a solution of silver nitrate containing 4·788 grms. per litre, each c.c. of which = $0{\cdot}001$ grm. chlorine may be used.

The alkalinity—that is, the power of neutralising an acid—is estimated by titrating 250 c.c. of the water with $\frac{N}{10}$ HCl and lackmoid, until the liquid turns just pink. It is usual to express the alkalinity in terms of calcium carbonate. (Note must be made of soluble alkaline carbonates if present ; see below.)

1 c.c. $\frac{N}{10}$ HCl = $0{\cdot}005$ grm. $CaCO_3$. No. of grms. $CaCO_3 \times 4$ = alkalinity in terms of calcium carbonate per litre.

Soluble Alkaline Carbonates (Na_2CO_3 and K_2CO_3).—250 c.c. of the water are boiled for half an hour in a porcelain basin. The liquid is cooled, poured into a 250 c.c. flask, and the basin well washed with cold, previously wellboiled, distilled water, the washings being received in the flask, which is then made up to the mark. The flask is shaken, and the liquid filtered through a dry filter. 200 c.c. of the filtrate are titrated in a porcelain basin with $\frac{N}{10}$ or $\frac{N}{100}$ HCl, using lackmoid as indicator until the liquid turns pink.

1 c.c. $\frac{N}{10}$ HCl = $0{\cdot}0053$ grm. Na_2CO_3. Wt. Na_2CO_3 found × 5 = grms. sodium carbonate in 1 litre.

Carbonic Acid, Combined.—500 c.c. of water are transferred to a porcelain dish and titrated with $\frac{N}{10}$ HCl, using lackmoid as indicator.

1 c.c. $\frac{N}{10}$ HCl = $0{\cdot}0022$ grm. CO_2.

Wt. $CO_2 \times 2$ = grms. combined carbon dioxide in 1 litre.

Carbonic Acid, Free, and as Bicarbonate.— This determination is of great importance for ascertaining the amount of lime or caustic soda required to be added in order to " soften " the water. Pettenkofer's method is recommended for this purpose.

100 c.c. of the water are put into a flask with 3 c.c. of a cold saturated solution of barium chloride, 2 c.c. of a solution of ammonium chloride, and 45 c.c. of a solution of barium hydrate of known strength. The flask is corked, the contents thoroughly shaken, and allowed to remain at rest for the precipitate of barium carbonate to subside ; 50 c.c. of the clear liquid are withdrawn, and titrated with $\frac{N}{10}$ HNO_3. The number of c.c. multiplied by 3, deducted from the number of c.c. required, to neutralise 45 c.c. of the barium hydrate solution employed for the determination, expresses the amount of carbon dioxide free, and as bicarbonate, in the liquid in terms of $\frac{N}{10}$ acid.

1 c.c. $\frac{N}{10}$ HNO_3 = $0{\cdot}0022$ grm. of CO_2 free, and as bicarbonate.

Example.—100 c.c. of water were treated as above. (45 c.c. of barium hydrate solution neutralised 31·5 c.c. of $\frac{N}{10}$ HNO$_3$). 50 c.c. of the clear solution (= one-third of the whole) neutralised 9·2 c.c. of $\frac{N}{10}$ HNO$_3$.

35·1 − (9·2 × 3) = 7·5 c.c. $\frac{N}{10}$. HNO$_3$, equivalent to free CO$_2$ in 100 c.c. of water.

∴ 0·0022 × 7·5 × 10 = 0·165 grm. carbonic acid free, and as bicarbonate in 1 litre.

WATER BLUE *v.* SOLUBLE BLUE.
WATER GLASS *v.* SODIUM SILICATE.
WATERPROOF FABRICS. This term is applied, on the one hand, to fabrics which are absolutely impervious to water — *e.g.*, Mackintosh, Willesden canvas, stiff felt hats, &c. ; and, on the other hand, to cloth which, while not rendered impervious, is capable of resisting a shower of rain ("rain-proof").

Woollen Fabrics.—There are three main processes in use.

Mackintosh cloth is prepared by coating the cloth with a thin film of gutta-percha, which may either appear on one side of the fabric or act as a cement between two layers of cloth, being in the latter case invisible.

Felt hats are rendered waterproof by two processes, distinguished as "water-proofing" and "spirit-proofing." In the former the hat body is impregnated with an alkaline (borax) solution of shellac or other resin, which is subsequently precipitated by acid and converted into a more or less continuous film in the interior of the felt by steaming and stoving. In "spirit-proofing," the resins, &c., are dissolved in alcohol, and after impregnating the felt, the solvent is removed by heat.

Rain-proof cloth is obtained by two principal methods :— 1st, Precipitation on the material of certain metallic oxides (or hydro-oxides) or insoluble salts, usually alumina or aluminium tannate with or without addition of soap, &c. ; 2nd, Impregnation with paraffin or other similar waxy substance.

Processes have also been introduced in which glue, gelatine, and other animal matters are employed, these being rendered insoluble by treatment with tannic acid, formaldehyde, &c.

Cotton Fabrics.— *Mackintosh fabrics* are produced as above described.

Willesden canvas has been treated under COTTON (*q. v.*), this process being specially suitable for heavy material—*e.g.*, tent cloths, awnings, cart covers, &c.

Alumina soaps, either alone or in conjunction with rubber, are also used, but have less importance in connection with cotton than with woollen material.

When used for wearing apparel the material should be so treated that the threads are rendered water-repellant, but the pores of the material should not be filled up, since it then becomes impervious to air, and is rendered unhealthful and unpleasant to wear.

WELD. The use of weld for producing a yellow colour upon fabrics was known in early times, this plant then, as now, growing wild in most European countries. It is thus of greater antiquity than most, if not all, other natural yellow dyes, and is still employed to a limited extent, although now of much less importance than fustic.

Origin.—Weld is the plant *Reseda luteola*, a gigantic species of *Reseda*, to which family also belong the common mignonette (*R. Odorata*) and the dock. The ordinary wild variety grows to a height of 3 to 4 feet, and has very much the appearance exhibited on a small scale by mignonette. The plant is cultivated in France, Germany, Italy, Austria, and to a small extent in England, being grown in Yorkshire along with the teazles so largely used in cloth finishing processes. A dwarf variety, which is said to be richer in colouring matter, reaches only about 18 inches in height. The plant is reared from seed, being planted in the early summer of one year and reaped in the autumn of the year following.

After being pulled up by the roots, the plant is carefully dried in the shade, tied into bundles, and sold without further preparation. Before being used, it is generally reduced to small pieces by means of a chopping or cutting machine, the roots being discarded.

An extract of weld, prepared in the same manner as logwood extract, also finds a limited application. The whole plant, with the exception of the root, contains colouring matter, but it exists most largely in the upper portion of the stem and the seeds. A decoction of weld, when freshly prepared, has a pale yellow colour. It quickly ferments, becoming turbid, and acquiring an unpleasant smell.

Colouring Matter of Weld.—Chevreul, who first isolated the pure colouring matter,[*] gave to it the name *luteolin*. It may be obtained by extracting the plant with alcohol, and precipitating the crude colouring matter with water. The greenish flocculent mass thus obtained is heated with pure water to 250° C. in a sealed tube, when, after cooling, crystals of pure luteolin are found in the upper portion of the tube.[†]

Luteolin is only slightly soluble in cold water or ether, but easily so in hot water or alcohol. It melts at 320° C., and sublimes at a higher temperature, with partial decomposition. Its molecular formula is uncertain. Schützenberger and Paraf give the numbers C$_{12}$H$_8$O$_6$, Moldenhauer C$_{20}$H$_{14}$O$_8$, and

---

[*] *Jour. de Chimie Médicale*, vol. vi., p. 197 (Paris).
[†] Schützenberger and Paraf, *Bull. de la Soc. Chim. de Paris*, 1862, p. 18.

WEIGHTS AND MEASURES.

I.—MEASURES OF LENGTH.

English Measures.	Equivalents in Metric Measures.
1 inch =	2·54 centimetres
12 inches = 1 foot =	30·48 ,,
36 ,, = 3 feet = 1 yard =	91·44 ,,
1760 yards = 1 mile =	1609·32 metres

Metric Measures.		Metre.		Yds.	Ft.	Ins.
Millimetre (mm) =		0·001	=	0	0	0·04
Centimetre (cm.) =		0·01	=	0	0	0·39
Decimetre (dm.) =		0·1	=	0	0	3·94
Metre (m.) =		1	=	1	0	3·37
Decametre =		10	=	10	2	9·71
Hectometre =		100	=	109	1	1·08
Kilometre =		1000	=	1093	1	10·79

(Equivalents in English Measures.)

II.—MEASURES OF SURFACE.

English Measures.	Equivalents in Metric Measures.
1 square inch =	6·45 sq. centimetres
144 ,, inches = 1 sq. foot =	9·29 ,, decimetres
9 ,, feet = 1 ,, yard =	0·836 sq. metres
4840 ,, yards = 1 acre =	0·4047 hectare
640 acres = 1 sq. mile =	25·4 hectares

Metric Measures.		Sq. metres.		Acres.	Sq. yds.
Centiare =		1	=	0	1·19
Are =		100	=	0	119·60
Decare =		1,000	=	0	1196·03
Hectare =		10,000	=	2	2280·33

(Equivalents in English Measures.)

III.—MEASURES OF CAPACITY.

English Measures.	Equivalents in Metric Measures.

For Solids—

1 cubic inch =	16·386 cub. cm.
1728 ,, inches = 1 cubic foot =	28·315 litres
27 ,, feet = 1 ,, yard =	764·505 ,,

For Liquids—

4 gills = 1 pint =	0·568 ,,
	(34·66 cub. ins.)
2 pints = 1 quart =	1·136 ,,
4 quarts = 1 gallon =	4·543 ,,
1 gallon = 70,000 grains	
1 gallon water = 277·29 cub. ins. = 10 lbs.	
1 cub. foot water = 6·25 gallons = 62·4 lbs.	
(about) = 1000 ozs. (nearly)	

Metric Measures.		Litres.		Cub. ins.		Galls.	Pts.
Cubic centimetre =		0·001	=	0·061	=	0	0·002
Centilitre =		0·01	=	0·610	=	0	0·02
Decilitre =		0·1	=	6·103	=	0	0·18
Litre =		1	=	61·027	=	0	1·76
Decalitre =		10	=	610·270	=	2	1·61
Hectolitre =		100	=	6102·705	=	22	0·08
Kilolitre =		1000	=	61027·052	=	220	0·77

(Equivalents in English Measures.)

IV.—MEASURES OF WEIGHT.

English Measures.			Equivalents in Metric Measures.
1 grain	=		0·0648 grms.
1 drachm	= 27·34 grains =		1·7716 ,,
16 drachms	=	1 ounce =	28·3456 ,,
16 ounces	=	1 pound =	453·59 ,,
14 pounds	=	1 stone =	6·52 kilogrms.
28 ,,	=	1 quarter =	12·63 ,,
4 quarters	=	1 cwt. =	50·50 ,,
(112 lbs.)			
20 cwts.	=	1 ton =	1016·048 ,,
(2240 lbs.)		=	10·16 quintals.

Metric Measures.		Grms.		lbs.	ozs.	drs.	grs.
Milligram (mg.) =		0·001	=	..	..	..	0·015
Centigram (cg.) =		0·01	=	..	..	..	0·154
Decigram (dg.) =		0·1	=	..	..	..	1·543
Gram (g.) =		1	=	..	..	..	15·43
Decagram =		10	=	..	..	5·64	..
Hectogram =		100	=	..	3	8·44	..
Kilogram (kilo.) =		1,000	=	2	3	4·38	..
Myriagram =		10,000	=	22	..	11·83	..
Quintal =		100,000	=	220	7	6·3	..

V.—CIRCULAR MEASURES.

Circle—

    Diameter   × 3·1416 = Circumference.
    ,,   squared × 0·7854 = Area.

Sphere—

    Diameter squared × 3·1416 = Surface area.
    ,,   cubed   × 0·5236 = Solid contents.

Cylinder—

    Diameter   × 3·1416 × length = Surface area.
    ,,   squared × 0·7854 × length = Solid contents

VI.—TABLES FOR CONVERTING

Metres into yards, &c.			Kilograms into lbs., &c.			Litres into galls., &c.		
M.	yds. ft.	ins.	K.	lbs.	ozs.	L.	galls.	pts.
1 =	1 0	3·37	1 =	2	3½	1 =	0	1·76
2 =	2 0	6·74	2 =	4	6½	2 =	0	3·52
3 =	3 0	10·11	3 =	6	9¾	3 =	0	5·28
4 =	4 1	1·48	4 =	8	13	4 =	0	7·04
5 =	5 1	4·85	5 =	11	0¼	5 =	1	0·8
6 =	6 1	8·22	6 =	13	3½	6 =	1	2·56
7 =	7 1	11·59	7 =	15	7	7 =	1	4·32
8 =	8 2	2·97	8 =	17	10¼	8 =	1	6·08
9 =	9 2	6·34	9 =	19	13½	9 =	1	7·94
10 =	10 2	9·71	10 =	22	0¼	10 =	2	1·6

Hlasiwetz, considering it to be an isomer of paradatisetin (v. QUERCITRON BARK) assigns to it the formula $C_{15}H_{10}O_6$. When melted with solid sodium hydrate, luteolin yields procatechuic acid and phloroglucin, and by the action of sodium amalgam on its acidified alcoholic solution, luteolin yields a purple colour similar to that produced under the same conditions by morin and quercitrin, to which substances, indeed, it is closely allied.[*]

Application.—Weld is employed in wool dyeing for the production of bright yellow shades, in conjunction with alum mordant; this being the purest and fastest yellow obtainable from natural colouring matters. Compound greens, known as "carriage greens," are produced by dyeing blue in the indigo vat, and subsequently topping with weld yellow.

WHITE LEAD *v.* LEAD (BASIC CARBONATE).

WHORTLEBERRY *v.* BILBERRY.

WILD SILK *v.* SILK.

WILLESDEN CANVAS *v.* COTTON (CELLULOSE).

WOLFRAM *v.* TUNGSTEN.

WOODRUF *v.* MADDER.

WOOD SPIRIT *v.* METHYL ALCOHOL.

WOOL. *Origin.*—Strictly speaking, wool is the hair of the sheep; but the hair of certain goats—*e.g.*, Cashmere, Mohair, and Alpaca—and of the camel are generally classed in the same category. Some naturalists assume that there are only three original species of sheep, viz. :—The *Ovis ammon* or *argali*, the wild sheep of Asia and America; the *Ovis musmon*, indigenous to the south of Europe and the northern parts of Africa; and the *Ovis aries*, or domestic sheep, which is the principal English variety.

From an industrial point of view Archer distinguishes no less than thirty-two different varieties of sheep, of which four belong to Europe, fifteen to Asia, eleven to Africa, and two to America. These varieties give different qualities of wool, which are distinguished from each other by the length, fineness, strength, elasticity, colour, curl, &c., of the fibres. Wool varies in quality not only in the case of different animals, but also in different portions of the fleece of one animal. The best quality is obtained from the shoulders, the lower part of the neck, the back, and the upper part of the sides, while that which covers the head, tail, belly, and legs is of an inferior quality. The separation of the various qualities of wool from each *fleece* can only be done by hand, the operation being known as *wool-sorting*.

The diameter of the fibre is, as a rule, proportional to its length—*i.e.*, the shorter the

staple the finer the fibre and *vice versâ*. The dyer usually distinguishes between the coarse and long-stapled *lustre wools*, most of which are produced in this country, and the finer qualities of *merino* or *cross-bred* wools, which are imported principally from Australia and the Cape, and are known under the general name of *Botany* wool.

In addition to these, the following should be specially mentioned :—

Cashmere wool of India, which is the product of a goat abounding in the mountains of Thibet. The hair of this animal sometimes reaches 18 inches in length.

Mohair, which is the wool of the Angora goat, is imported into this country chiefly from Turkey and the Cape. Mohair is characterised by its striking lustre.

Alpaca, the hair of a goat which belongs to a genus of which the llama is the best known species. Closely allied to this is the so-called *Vicuna* wool.

Camel's Hair.—Camels, which abound as domestic animals in many hot climates (especially in the northern parts of Africa), cast their hair periodically; this is collected, and comes into the market as a textile material.

Fur consists principally of the hair of the hare and the rabbit, and is extensively employed in the manufacture of felt for hats.

The wool of diseased sheep, or of such as have died from disease, is of inferior quality to that taken from the healthy living animal. It also behaves differently in dyeing. Bosc gives an interesting account of an experiment carried out by him with the wool of three Rambouillet sheep of the same age. The first was in robust health, the second diseased, while the third had died of disease. Each fleece was washed separately and spun into yarn. The yarn was made up into hanks and dyed at the Gobelins in three shades, viz. :— blue, red, and yellow. The colour of the hanks made from the wool of the healthy sheep were bright, of the diseased sheep of a lighter shade, and those from the dead sheep dull. In dyeing each colour, all three samples were dyed in the same bath. The wool from slaughtered sheep, if removed from the skin by cutting, is not inferior in quality to that shorn from the living animal. The usual process for removing the wool from the skins is, however, to steep the latter for a time in lime water or dilute solution of sodium sulphide, which causes the fibres to become so loosened at their roots that they can be readily removed. Wool obtained in this manner is generally known as "pulled wool," and is inferior in quality to that obtained from the living animal.

According to its length of staple, wool is generally divided into "long-stapled" and "short-stapled" qualities, long-stapled wool (exceeding $1\frac{1}{2}$ inches in length) being usually

* Luteolin has quite recently been produced synthetically by Kostanecki (*Bull. Soc. Chim. Mulhouse*, 1901, pp. 35-41).

subjected to the process of combing, made up into *tops*, and afterwards spun on ring or cap spinning frames into *worsted yarn;* the shorter qualities being carded and spun on mule spinning frames into *woollen yarn.* Worsted yarn is principally used in the manufacture of coatings, worsted trouserings, and ladies' dress goods, which require little or no milling. Woollen yarn, on the other hand, is used principally in the manufacture of goods which are subsequently milled for the purpose of producing, to a greater or less degree, a felting of the fibres. In worsted yarn the fibres lie more or less parallel to each other, and the diameter of the yarn does not vary much, while in woollen yarn the fibres cross each other in all directions, and the diameter of the yarn is very irregular.

Counts.—In worsted and Mohair yarns the counts indicate the number of hanks of 560 yards each to the pound.

For woollen yarns there is no uniform system. In Yorkshire the counts generally indicate the number of yards per drachm, but in Dewsbury they indicate the number of yards per ounce. In the West of England the woollen counts indicate the number of hanks of 320 yards each to the pound.

PHYSICAL STRUCTURE.

The root of the wool fibre is enclosed in a sort of minute bag or sack, formed by a convolution of the skin. This receptacle is termed the *hair follicle.* In the skin itself there are four distinct layers, the outermost of which is the *scarfskin* or *cuticle.* It consists of the dried up or dead cells of the underlying *epidermis* or *rete mucosum,* which is the true skin. The third layer from the surface is termed the *papillary layer,* which is filled with a network of minute blood-vessels, glands, and nerves ; and underneath this again is the *dermis* or *corium,* in which exist certain globular masses which under the microscope have the appearance of bunches of grapes. These are the *adipose cells,* the function of which is to throw off moisture which is carried by the *sudoriparous glands* to the surface, where it is eliminated as perspiration. Certain pear-shaped receptacles which terminate in the hair follicle near its orifice, are the *sebaceous glands,* which exude a greasy substance which adheres to the surface of the fibre. This is known as *yolk* or *suint,* and in the natural economy of the animal serves as a lubricant and preservative of the fibre. It is subsequently removed during the wool-scouring process.

The embryo hair in the follicle is produced by the exudation of a plastic lymph which gradually becomes granular or cellular. By the multiplication of these cells in the globular extremity of the follicle, the fibre is gradually pushed up or grows out of the tube of the follicle until it reaches, and eventually projects from, the surface of the skin. There is little doubt that the original cells composing the fibre are all of the same spherical form, the peculiar structural formation of the fibre being largely governed by the shape of the follicle. It will readily be seen that if a mass of semi-plastic spheres (representing the cells) are forced up a tube of diminishing diameter (the follicle) the spheres will be deformed by lateral pressure, becoming elongated and of smaller diameter. Friction will cause this effect to be greater at the sides of the tube, the now spindle-shaped cells being there more or less completely flattened into plates. Aggregations of these flattened plate-like cells take the form of lustrous horny scales, which constitute the outer bark or covering of the fibre. The scales, which have been compared to the scales of a fish or to the slates on a house-top, overlay each other in the manner which the comparison suggests, the free edges protruding more or less from the bulk of the fibre, while the lower or covered edges are imbedded and held in the inner layer of spindle-shaped cells. The free edges invariably point away from the root of the fibre just as do the bracts of a fir-cone.

The fact that the surface of the fibre is of a serrated or scaly character is readily proved by gently rubbing a wool or hair fibre between the finger and thumb, when it will always travel in the direction of the root of the fibre.

Situated centrally along the axis of the fibre there is usually a well-marked core or pith, termed the *medulla* or *medullary canal.* This is composed of cells which have retained more or less their spherical character, and to a certain extent their plastic nature.

Three separate portions may thus be distinguished in the wool fibre :—(1) A central cavity filled with comparatively soft and approximately globular cells ; (2) surrounding this and forming the larger portion of the fibre, a thick layer of fibrous or spindle-shaped cells ; (3) an outer casing of flattened horny scales.

When viewing a transverse section of a wool fibre, there is no sharp line of division between the three portions indicated above, the change from one to another being quite gradual. The separation into zones, though well marked, is therefore indefinite as regards boundaries. The physical properties of wool, which render it of such value as a textile fibre, are intimately connected with, in fact are dependent upon, the peculiar structure which has just been described.

VARIATIONS IN PHYSICAL STRUCTURE.

When such apparently dissimilar things as the wool of the sheep, human hair and finger

nails, birds' feathers, and horses' hoofs are all of very similar composition, and differ only in structural arrangement, it does not seem improbable that wool fibres should vary somewhat in themselves. This also is actually the case ; fibres from different breeds of sheep, or even from different parts of the same animal, vary greatly, not only in length, thickness, &c., but also in actual structure. A typical fibre, such as may be obtained from a good merino or Southdown fleece, will possess the typical structure described above, but frequently the type is departed from to such an extent that the central core of globular cells is entirely absent. The serrated character of the outer cells also reaches a much higher state of development in some samples of wool than in others.

PHYSICAL PROPERTIES OF WOOL.

It is very interesting, as well as instructive, to examine the various characteristic properties of wool in the light of the peculiar structure of the fibre, which has already been described. The physical properties of wool which render it of such value as a textile matérial are—(1) Strength and elasticity, (2) curliness, (3) felting property, (4) lustre, (5) avidity for liquids.

Each of these properties should receive careful attention and thought during all stages of manufacture, so that it may be utilised to the fullest extent in the process which is being carried out, or preserved uninjured either for use in some subsequent process, or to enhance the value of the finished article.

(1) *Elasticity and Strength.* — These are properties which, in common with silk, wool possesses in a greater degree than the vegetable fibres.

When submitted to *torsional* strain the wool fibre exhibits a remarkable strength, and when the breaking point is reached the fracture always takes place at the juncture of two rings of the outer scales, the imbedded edges of the lower layer being pulled out of their seats. The scales themselves are never broken.

By reason of its structure, wool is able to withstand an enormous *crushing* strain; in fact its resistance is so great that for all practical purposes the effect of any direct pressure may be neglected. The structure again is beautifully adapted to prevent injury by *flexure*. When any elastic body is subjected to a bending strain, compression is produced on the inner surface of the bend and a torsional strain on the outer surface. In the wool fibre, the cells in the central zone being more or less plastic, are, no doubt, temporarily deformed, the spindle-shaped or fibrous cells are bent, and the outer scales being free for a portion of their length, slide over one another to the extent necessitated by the degree of flexure. When the strain is removed the central or medullary cells tend to assume their spherical shape, the fibrous cells to straighten themselves, and the outer scales to resume their original position, thus causing the fibre to straighten. The same remarks adequately explain the behaviour of the fibre as an elastic body, when stretched. It has been found that the limit of elasticity is from 0·3 to 0·5 per cent. of the length, and if stretched beyond this amount the fibre will not return to its original length, but takes a permanent set; the strength of the fibre is then much impaired, mechanical disintegration having, no doubt, commenced. This is well seen by stretching a white horse-hair, the sudden change from a semi-translucent to an opaque appearance marking the period when the elastic limit is exceeded. The breaking strain of the wool fibre depends a good deal upon its diameter, (which varies considerably), and is usually between 15 and 35 grms. ($\frac{1}{2}$ oz. to $1\frac{1}{4}$ ozs.). Both the breaking load and the elastic limit are, however, very variable quantities, and are often unequal in different parts of the same fibre. It has also been found that the amount of moisture which the fibre contains at the moment has a certain influence on the strength and elasticity. These valuable properties of the fibre are, of course, injuriously affected by any process which tends to modify its structural arrangement, or act upon the fibre substance ; and the various substances used in manufacturing processes behave very differently in this respect.

The strength and elasticity of the fibre are very important factors in the spinning and weaving processes, and it is not too much to say that the milling or felting process could not possibly be conducted in the manner usually employed if the elasticity of the fibre were not capable of taking up the original sudden strain produced by the blow or pressure.

(2) *Curliness.*—The curly, wavy, or twisted character of wool is caused by the unequal contraction of the surface of the fibre, and depends in a great measure upon its hygroscopic nature. The curl may temporarily be entirely removed by wetting the fibre in hot water and drying in a stretched condition, or may be artificially induced by unequal drying—a fact which is turned to practical account in the curling of feathers and of hair. The amount of curl in different samples of wool is very variable, being, as a rule, greatest in the finer qualities, and only slightly developed or even entirely absent in coarser varieties. The diameter of the wool fibre varies from $\frac{1}{2000}$ to $\frac{1}{500}$ inch, and the number of curls from 30 per inch in fine wool,

to 1 or 2 in the thicker fibres. The property of curliness is most valuable to the spinner, since it enables him to produce a much finer thread than would be possible in its absence; and by reason of the greater development of curl in wool than in cotton, it is possible to spin a thread containing fewer fibres with the former than with the latter. The curl has also a considerable, though not a principal, influence in the milling process.

(3) *Felting Property.*—The property possessed by wool and similar fibres, of felting together to form a commercially valuable fabric, is quite distinctive; silk and the vegetable fibres being incapable of producing such a material. Historically, felting is a much older process than spinning and weaving, a fact of which it is not difficult to give an explanation. Primitive man, clothing himself in skins to which the hair was adhering, would find that in process of time the hair became matted together into a compact mass, especially where it was most subjected to pressure and friction. In an extreme case it might have occurred that the matting together of the hair had gone so far that by cutting it away from the skin a garment of felted hair would be obtained; and it would then be but a small step to produce such a material by purposely applied pressure and friction upon previously shorn hair or wool. In this way the manufacture of felt would naturally long antedate the much more complicated and less obvious processes of spinning and weaving.

The felting property of wool depends primarily upon the scaly or serrated character of the outer surface of the fibre, but is also influenced, as already mentioned, by its curliness and elasticity. With regard to the action of the latter, in addition to its use in preventing the destruction of the fibre by the sudden strains induced during the process, the elasticity has a direct effect in aiding the felting, because it is evident that if a bundle of elastic threads were alternately stretched and freed, pounded, released, and rolled about, they would become entangled into a more or less coherent mass. Considering again, for a moment, the action due to the curly nature of the fibre alone, it is equally obvious that a mass of watch hair-springs would become inextricably entangled if treated in a similar manner. In order to understand the action of the fibre surface it is necessary to remember that the outer scales have protruding free edges, which always point away from the root of the fibre. If two fibres, therefore, are placed parallel to each other, root to root and tip to tip, they may, even when pressed together, be drawn over each other in either direction; but if one of them is turned, so that the fibres lie in opposite directions, and the process is then repeated, the fibres will slide over each other readily if the root end of either is drawn, but will refuse to move if compressed and the tip end of one is pulled. The reason is that in the former case the free edges of the scales of one fibre slide over those of the other, but when drawn in the reverse direction they interlock, causing movement in that direction to be impossible.

It is now easy to see that in the early stages of the felting process the curl and the elasticity are the principal causes of the matting together of the fibres, the necessary conditions for the interlocking of the scales— *i.e.*, contiguity and partial parallelism of the fibres in reverse directions, combined with pressure, not obtaining to a great extent. As the process proceeds, however, and the mass of fibres becomes denser, the number of parallel contacts increases, the action of the scales becomes more and more pronounced, and in the later stages is all-important. That the curliness of the fibre is not, as is sometimes thought, the principal cause of felting, is evident from the fact that some varieties of wool, which are almost without curl, will felt quite readily; while, on the other hand, others—of which mohair is an example—possess a well-developed curl, and yet felt with difficulty. This fact is turned to practical account in the production of some "curl" and "crepon" cloths, in which wool and mohair are combined together in a woven fabric, which is afterwards milled. The wool then felts together and contracts, leaving the mohair in slack threads, which, by reason of the twist in the thread, form little bunches or curls. Alpaca and mohair partake both of the nature of wool and hair. They resemble wool in curliness and fineness of fibre, but are allied to hair in the almost entire absence of free edges to the outer scales; and this is the reason why the mohair does not felt.

Other things being equal, the wool containing the largest number of scales per inch will be the best felting wool; but the most important point is that the scales should have free protruding edges. The reason why "skin" wool felts more easily than "fleece" wool, is to be found in the fact that in the former, the lime or other substance used in the process of removing the wool from the skin, has caused the scale edges to protrude to an abnormal extent. This indicates that by the action of certain agents the felting property may be increased, which is, of course, a well-known fact. By adding some acid or alkaline salt to the water used in the milling or felting process, or even by using hot instead of cold water, the scales are caused to stand out more prominently, and the felting action is increased. The greatest possible effect in this direction is produced

by milling in a hot acid solution, and to such an extent may the process be then carried that the felt almost acquires the density of wood, and may be sawn and turned in the same manner. Such felt is used for polishing glass and jewellers' work. Felt hats are also made by felting or "planking," as it is termed, in an acid solution. A microscopical examination of a piece of hard felt shows that the outer scales of the fibre have lost their plate-like form and become partially distended. The fibres also have become conglomerated and welded together in such an intimate and permanent manner that it is difficult to distinguish their individuality. It is evident then, that when pushed to its extreme limits, the felting process brings into play the slightly plastic nature of wool, the fibres being more or less completely cemented together. The ordinary milling process, however, as carried out in cloth manufacture, is of a much less severe character, the integrity of the fibres being maintained, and the flat, horny nature of the outer scales being injured as little as possible; since it is upon the retention of this that the lustre of the finished fabric largely depends.

To sum up in a few words, it may be said that the essentials for carrying out the felting process are, a wool having a certain elasticity and a large number of well-developed outer scales, which must be submitted to intermittent frictional pressure in the presence of water; the process being accelerated by heat, acids, or alkalies.

(4) *Lustre.*—This quality, in respect of which wool holds a position intermediate between cotton and silk, is due to the reflection of light from the horny outer sheath of the fibre. Of all the physical properties of the fibre it is the most variable in degree, alpaca and mohair surpassing all other varieties in this respect. The texture of the outer scales in different qualities of wool varies considerably; under the microscope some have the appearance of polished ivory, others look like porcelain, while some fibres possess scales which may be compared in appearance to clear, slightly-tinted glass. The effect, however, largely depends upon the method of observation; the same fibre appearing very different when viewed as an opaque and as a transparent object, and under different illuminations, &c.

For the maximum amount of lustre it is above all things necessary that the outer surface of the individual scales or plates should be polished and glassy. Anything which tends to pit or roughen the scales will, of course, destroy the optical continuity of the reflecting surface, thereby causing dispersion of light, and consequent diminished lustre of the fibre; and since all liquids do this in greater or less degree, the property of

lustre is most difficult to maintain throughout the manufacturing processes.

It should be generally recognised that acid or alkaline solutions, or even pure water,* are capable, under certain conditions, of actually *dissolving* the wool substance; and they undoubtedly attack the fibre to some extent during the course of an ordinary scouring or dyeing process.

The lustre of the fibre is not only injured by processes in which solutions are employed, but it is also deteriorated by an excessively great, or too long-continued, heat.

Of all the valuable attributes of the wool fibre, lustre is therefore the most easily destroyed, and the degree to which it is retained in the finished article depends largely upon the care and skill brought to bear in the different treatments to which the fibre is necessarily subjected during its manufacture into cloth.

(5) *Avidity for Moisture.*—Wool is very hygroscopic, readily absorbing moisture from the atmosphere and retaining it tenaciously. Under average conditions the fibre contains about 14 per cent. of its weight of moisture; but the amount is greatly influenced by the hygrometric condition of the atmosphere. In addition to surface condensation the moisture is, in all probability, located actually within the individual cells, since the membranous cell walls are permeable to water. This is no doubt the reason why it is so difficult to drive off the whole of the water, it being in fact impossible to remove the last portion of the moisture without partial disintegration of the fibre.

By drying wool at 50° C. (120° F.) a loss in weight of from 7 to 10 per cent. takes place, and on raising the temperature to 100° C. (212° F.) a further loss of 5 to 8 per cent. occurs. After drying at 50° C. the wool will again absorb moisture from the atmosphere up to the original amount, but when dried at 100° C. only part of the loss is regained, showing that some change has taken place apart from the mere loss of moisture. This view is supported by the fact that wool heated for a long time at a temperature considerably below 100° C. gradually acquires a yellow colour, becomes lustreless and brittle, and is much reduced in tenacity and strength.

To account for these effects Bowman suggests that the water exists in the fibre in two conditions—*i.e.*, as moisture, and as chemically combined water of hydration. But it appears reasonable to reserve a definite opinion on this point until the chemical constitution of the fibre has been determined.

This question of the drying of wool is one of much greater practical importance than is commonly supposed. Wool dried in the open

* See p. 364.

air will always yield an article of higher quality than can be obtained from the same wool when dried by means of artificial heat.

A case in point was recently brought under our notice by a manufacturer of felt hats, who stated that he could always produce a better quality hat in summer than in winter from the same raw material. Inquiry elicited the fact that it was the practice in these works to dry the hat bodies in the summer by placing them in an open shed, whereas in the winter season they were dried, at several stages of the manufacture, over the steam boilers. This fact sufficiently explained the variable result obtained.

Although it is important that wool should be dried at as low a temperature as possible, it is of much greater importance that the fibre should not be submitted to the action of dry heat; that is to say, the drying process should not be continued after the moisture has all been evaporated. In fact, to put it another way, one may say that practically no injury is sustained, even with a considerable degree of heat, *so long as moisture is being given off*, but immediately moisture ceases to be evolved the deterioration above mentioned commences.

Chemical Composition of Wool.

When treating of the structure and mode of growth of the fibre it was pointed out that certain glands situated beneath the skin of the animal exude a greasy substance, which, coating the fibres to a considerable thickness, serves to protect them from injury. The amount of this encrusting substance is very variable, and on the raw fibre it is always associated with more or less sand, dirt, and other foreign matter; the proportion of pure wool fibre in different samples of raw wool is therefore equally variable, as is shown by the following analyses, which, however, do not, by any means, represent extreme cases:—

Analyses of Raw Wool (after drying at 100° C.).

	No. 1.	No. 2.	No. 3.
Moisture,	6·26	10·4	8·2
Sand, dirt, &c.,	11·13	3·1	20·1
Yolk (greasy matter),	47·30	27·0	40·5
Pure wool,	35·31	59·5	31·2
	100·00	100·00	100·0

In order to estimate accurately the amount of pure wool in a sample of raw wool, a weighed quantity of the latter should be dried at 100° C. and then successively treated with (1) ether, (2) water, (3) alcohol, and (4) dilute hydrochloric acid; then washed, dried at 100° C. for a short time, and weighed. Speaking generally, the finer varieties of wool contain a larger proportion of yolk than the coarser and less valuable sorts.

Pure wool fibre, in common with hair, is chemically the most complex of textile fibres. Cotton being a carbohydrate, is composed of but three elements — carbon, hydrogen, and oxygen; these elements being present in the proportion represented by the formula $C_6H_{10}O_5$. In the silk substance an additional element, nitrogen, is found; the molecule at the same time being more complex, as is shown by the formula given for fibroin, $C_{15}H_{23}N_5O_6$. Wool contains still another constituent, sulphur; and the simplest formula which will at all conform to the percentage composition contains thirty-nine atoms of carbon. It has been considered that the wool fibre consists of a definite chemical compound (keratine), to which the formula $C_{39}H_{65}N_{11}SO_{13}$ has been given; but this view is probably incorrect, the fibre being more likely composed of a mixture of at least two, and possibly several, closely allied very complex substances. It is possible, and even probable, that the outer epidermal scales have a different composition to the rest of the fibre; but whether this is the case or not, it is now considered with some degree of certainty that wool is not a simple definite chemical compound. This at once accounts for the discrepancy observed in the figures obtained by ultimate analysis, the following figures giving an indication of this extent of the variation:—

Percentage Composition of Pure Wool Fibre.

	Marcke and Schültze.	Mülder.	Bowman.
	per cent.	per cent.	per cent.
C,	49·54	50·5	50·8
H,	7·29	6·8	7·2
O (by difference),	24·13	20·5	21·2
N,	15·60	16·8	18·5
S,	3·44	5·4	2·3
	100·00	100·0	100·0

In addition to the above constituents, there is always present in wool fibre a small quantity of mineral matter, amounting frequently to between 1 and 2 per cent., and consisting principally of salts of potassium, calcium, iron, and aluminium, with traces of silica, phosphorus, &c. The character of this mineral matter is, no doubt, largely determined by the nature of the soil upon which the sheep has been pastured.

It will be seen on referring to the analyses of wool which are given above, that sulphur

is by far the most variable constituent, sometimes as little as 1·5 per cent., and occasionally as much as 6 per cent. being found. It appears, as was first pointed out by Chevreul, to be present in two different conditions—one portion being in the free state, or only in feeble combination; while the remainder, which (according to Knecht) amounts to about 30 per cent. of the total sulphur, cannot be removed without entire disintegration of the fibre. The sulphur in feeble combination very readily forms sulphides if the wool is brought into contact with metals; and dark coloured stains are frequently produced in this manner. The formation of black sulphide of lead, when wool is heated with a solution of plumbite of soda, serves, indeed, as a test to distinguish wool and hair from all other fibres, since the two former fibres alone contain sulphur.

In order to guard against the formation of these stains, it is sometimes necessary to remove the active sulphur from wool which is intended for white or delicately coloured goods, and this may be done by steeping for twenty-four hours in milk of lime, and subsequently washing, then treating with dilute hydrochloric acid to remove the lime, and again washing in water.

That portion of the sulphur which cannot be removed by this treatment is evidently in a different state of combination, since it will not form sulphides, and does not, therefore, produce a black colour with plumbite of soda.

With regard to the chemical *constitution* as apart from the *composition* of the fibre, little is known. When submitted to dry distillation (heated without access to air) wool yields first sulphuretted hydrogen and a little carbon disulphide, then ammonium carbonate, and afterwards pyridine, acridine, &c., and a residue of carbon.

Schützenberger also obtained nitrogen, carbon dioxide, oxalic and acetic acids, leucine, and tyrosine on heating wool with barium hydrate; and these decomposition products tend to show that wool is, or at any rate contains, an albuminoid.

An interesting series of experiments bearing upon the chemistry of wool has been made by Knecht.[*] On heating purified wool with sulphuric acid he obtained a light brown solution which readily gives precipitates with solutions of the acid colouring matters. The substance which produces these precipitates or lakes, he considers to be identical with the constituent of the fibre which combines with the acid colours in an ordinary dyeing process, the amount of this lake-forming substance being from 25 to 30 per cent. of the wool.

To obtain the above-mentioned acid solu-

* *Journ. Soc. Dyers and Col.*, August, 1888.

tion of wool, 100 parts of the fibre are boiled for about two hours with 200 parts of strong sulphuric acid diluted with 300 parts of water. The wool gradually dissolves, producing a brown solution, which, when neutralised by alkali, deposits a yellowish-white precipitate consisting of the lake-forming substance.

A body called *lanuginic acid* was previously known, being produced by a process the converse of that above described—*i.e.*, by dissolving wool in caustic soda and neutralising with acid. Knecht found that an acid solution of lanuginic acid has exactly the same properties as his lake-forming substance, and therefore considered the two to be identical. Campion, who originally prepared lanuginic acid,[*] gave its composition as $C_{38}H_{60}N_{10}O_{20}$, but Knecht states positively that it contains sulphur in the inactive condition.

Lanuginic acid not only possesses basic properties, as indicated by its forming compounds with acid colouring matters, but also shows well-marked *acid* properties, giving precipitates with both metallic hydrates and basic colouring matters. It is thus an *amido acid*, the acid group apparently being stronger than the basic group, since wool dissolves more readily in alkali than in acid.

It is further considered that lanuginic acid is an albuminoid, since it gives the characteristic reactions of that class of bodies.

Knecht does not consider that lanuginic acid exists as such in wool, but that it is a simple decomposition product. This idea is borne out by the fact that wool will not combine with the free sulphonic acid colouring matters, excepting in the presence of free acids; this is to say, since the acid colouring matters are always used in the form of sodium salts, a large excess of acid over and above that required to liberate the free sulphonic acid must be added to the dye-bath. If the wool is *previously* boiled with sulphuric acid it may, however, be dyed direct with free sulphonic acids. Coupled with the above, the fact that wool itself will dye from a colourless solution of rosaniline base, again shows the superior activity of the acid groups it contains.

Richard[†] thinks that the behaviour of wool towards colouring matters and mordants may be explained—as is generally admitted —by the supposition that it contains an amido acid. He has attempted to prove the existence of an amido group by treating wool with nitrous acid and then with an alkaline solution of some phenol (phenol, resorcinol, naphthol, &c.). He thus obtained various brown and red colours upon the wool, which are possibly azo colours, the wool substance itself entering into the composition of the

* *Comptes rendus*, vol. lxxii., p. 330.
† *Proc. Soc. de Mulhouse*, January, 1888.

colour. However, as Richard himself points out, if the substance obtained on treatment with nitrous acid is a diazo compound of languinic acid (or other constituent of wool), it possesses properties differing from those usually associated with diazo compounds, since by treatment with boiling hydrochloric acid it is not decomposed but is still capable of giving colours with the phenols.

Breinl [*] has made some very interesting experiments which, though not bearing directly upon the constitution of the fibre, may conveniently be noted here, since, taken in connection with the above remarks, they have an important practical significance. He found that if woollen cloth is splashed with alkali or acid and then heated (dried or steamed), the portions which are thus treated will dye a much darker shade than the rest of the fabric ; and he points out that this is probably a frequent cause of irregular dyeing. In all probability the action is a twofold one, partly chemical and partly physical. It is evident from what has been already stated that in those places splashed with acid or alkali there will be a liberation of active languinic acid ; and the reagents will also tend physically to open or raise up the outer scales of the fibre, thus giving the dye solutions freer access to the inner and more easily dyed portion.

Colouring Matter of Wool.—The natural colour of wool varies from white to dark brown or almost black ; but with regard to the colouring substance little is known. Iron or manganese is always present in the ash of dark wool, and magnesia is frequently found in light coloured samples ; but in all cases an oily organic matter of a similar colour to that of the wool may also be extracted, and it is uncertain to what the colour of the wool is actually due.

Chemical Properties of Wool.

The animal fibres—silk, wool, fur, and hair—are chemically of a much more active nature than cotton and other fibrous vegetable products, that is to say, speaking generally (for there are important exceptions), they more readily combine with, or are affected by, chemical reagents.

Action of Water.—The action of moisture on the fibre has already been incidentally alluded to ; and although, as Gardner has shown,[†] pure water at a temperature of about 400° F. is capable of actually dissolving wool, the only noticeable effect on boiling the fibre in water for a reasonable length of time is a diminution in its lustre.

Much more destructive is the action of steaming. Scheurer[‡] states that "by steam-

ing thoroughly cleansed woollen cloth at a temperature of 210° F. the fibre is weakened to the extent of 18 per cent. in three hours. The destructive action then becomes less, and equals 12 per cent. for each successive interval of twelve hours, the total weakening effect amounting in sixty hours to 75 per cent. of the original breaking strain—a destructive effect equal to that produced on cotton only after 420 hours steaming."

Action of Acids.—Wool absorbs acid from solution with much avidity, and retains it with considerable tenacity. It is not yet established whether the whole of the acid withdrawn from solution exists in chemical combination with the fibre or some constituent of the fibre ; but that a portion, at any rate, does so is evident from the fact that on long continued washing, part of the acid is removed *as an ammonium salt*, the ammonia being eliminated from the fibre substance itself. No doubt, however, the cellular structure of wool, which determines its very absorbent nature, has something to do with the difficulty found in removing the acid by washing.

Acetic acid and organic acids generally have very little chemical action on wool under any conditions of practical work, but dyeing defects may possibly arise if these solutions are allowed to concentrate upon the fibre. Acetic, oxalic, and tartaric acids are all frequently used in dyeing operations.

Sulphuric acid, if sufficiently concentrated, will, as has been already mentioned, dissolve wool. This effect requires acid of 25 to 30 per cent. strength—say, 45° Tw. Much more dilute acid than this will, however, exert an injurious action, the safe limit being about a 6 per cent. solution of acid (10° Tw.). Very prolonged boiling with even a 3 per cent. solution of sulphuric acid will, however, weaken the fibre. The most easy and definite method of determining whether the fibre has sustained serious injury is afforded by a microscopical examination, which will show in this event that the outer scales have been raised up, and protrude abnormally from the body of the fibre, or even, in extreme cases, that they have been entirely removed.

Hydrochloric acid has a similar action to sulphuric acid—*i.e.*, its effect if dilute is negligible, but when concentrated it entirely dissolves the fibre.

Nitric acid behaves differently to sulphuric or hydrochloric acid. When heated with dilute nitric acid, wool, like all skin products, becomes permanently coloured yellow. This action is not thoroughly understood, but the common statement that the yellow colour is due to a production of picric acid is certainly incorrect. Colouring matters, almost without exception, are destroyed by a treatment with boiling

---

[*] *Zeit. für ang. Chem.*, December, 1888.
[†] *V. Wool Dyeing*, p. 29.
[‡] *Bull. Soc. Ind. Mulhouse*, 1893, p. 89.

dilute nitric acid, and since the wool fibre is little affected thereby, save for the production of the above-mentioned yellow colour, this process is frequently resorted to for " stripping off" the colour of dyed material previous to re-dyeing.

Sulphurous acid, when cold and dilute, has no appreciable action upon the fibre, but tends to remove the pale yellow colour which so-called white wool always naturally possesses. It is, therefore, largely employed as a bleaching agent for wool.

Hypochlorous acid, which, in the form of bleaching powder, is the bleaching agent *par excellence* for cotton and vegetable fibres generally, cannot be employed for bleaching wool, because it tends to develop rather than to remove the yellow colour. It is found, however, that wool which has been treated with a solution of bleaching powder or hypochlorous acid possesses a greatly increased affinity for most colouring matters; and this fact, which was first noticed by Mercer, is turned to practical account in the printing of mixed wool and cotton goods, the dyeing of skin mats, &c., the effect apparently being due to an oxidation of the fibre.

Chlorine gas in aqueous solution acts in a similar manner to hypochlorous acid, but more energetically. The very considerable action of extremely dilute solutions of chlorine is probably due to the power which wool possesses in a marked degree of *concentrating* or condensing *upon itself* any reagent with a solution of which it is brought into contact. There is no doubt that this action comes into play largely in mordanting and dyeing processes.

Action of Alkalies.—It has been mentioned that the action of acids upon cotton is, on the whole, much more destructive than is the case with wool. With regard to alkalies and alkaline salts the position of the two fibres is reversed; for while cotton may be boiled with a solution of carbonate or caustic soda with impunity, such a treatment would be absolutely destructive to wool.

Caustic alkalies (caustic soda or potash) should never be brought into contact with wool. Even when cold and dilute they exert a powerful detrimental effect. A solution containing 2 per cent. of caustic soda will dissolve wool completely by boiling for a short time, cotton being unaffected thereby; and this affords a simple means of estimating the respective amount of the fibres in a mixed fabric.

Buntrock * has, however, recently shown that a very concentrated solution of caustic soda (90° Tw.) actually strengthens wool, causing it also to exhibit an increased affinity for colouring matters.

Ammonia has little action on wool, though

* *Farber Zeitung*, 1898, No. 3.

in common with all alkaline solutions it has a great tendency to reduce the lustre of the fibre.

Alkaline carbonates, such as the carbonates of soda, potash, or ammonia, have very much less injurious action than the caustic alkalies. When used in dilute solution, and at a low temperature, they have indeed little effect, and are the chief agents used in removing the yolk or suint from the fibre in the scouring process.

Soaps, when pure, act in a similar manner to alkaline carbonates; but care must always be taken that the scouring agents employed are free from *caustic alkali*, soda ash and soft soap being especially liable to contain this impurity.

Action of Metallic Salts.—When wool is boiled with a solution of certain metallic salts a dissociation of the latter takes place, the metal probably as a basic salt combining with, or being deposited upon, the fibre in an insoluble condition. A portion of the acid is also taken up by the wool, while another portion is left in solution, partly in the form of an ammonium salt ; the liberation of ammonia from the wool being probably an important factor in determining the fixation of the metal. Upon these facts the mordanting of wool depends, the fibre being boiled in a solution containing the sulphate, chloride, &c., of aluminium, tin, chromium, iron, &c., as the case may be.

Behaviour towards Colouring Matters.—Wool, of all textile fibres, exhibits the most powerful affinity for the colouring matters. It combines directly with all the substantive dyes, and can be readily dyed with them. Its affinity for these is generally greater than that of silk ; in other words, the colours produced on wool resist the action of boiling water or of soap better than those on silk. Thus, if wool and silk are dyed the same shade with naphthol yellow or indigo extract, and then boiled with water, the colour is extracted from the silk much more rapidly than from the wool. There are some exceptions to this rule, and on these facts is based the principle of dyeing the wool and silk in mixed goods manufactured from these two fibres, two entirely different shades in one bath. As shown by Hirsch,* wool also evinces a strong affinity towards certain substances, like the naphthol sulphonic acids, which are not dyes in themselves but are capable of forming dyes by subsequent treatment. Thus wool, boiled in acid solution with 1 to 2 per cent. beta-naphthol disulphonic acid R, became orange when passed into a solution of diazotoluene, after the addition of ammonia. In a similar manner, naphthol green may be produced on the fibre, by boiling in naphthol mono-

* *Journ. Soc. Dyers and Colourists*, 1889, p. 115.

sulphonic acid, passing through an acidulated bath of nitrite of soda and then into a hot copperas solution.

For some adjective dyes, such as the insoluble red dyewoods and catechu, wool also exhibits a direct affinity. Others, like alizarin, which are used in dyeing in the form of pastes containing the colouring matter in a very finely-divided state, are, when used without mordant, absorbed mechanically and fixed loosely by the fibre.

The various qualities of wool behave differently in dyeing, the finer qualities generally requiring more dyestuff to produce a given shade than the coarser ones. The amount of dyestuff required also varies according to the state in which the wool is dyed—as loose wool, slubbing, yarn, or in the piece—the former requires most, the latter least, dyestuff.

Certain kinds of wool, e.g., mohair, are sometimes very difficult to dye; they appear to take up only a very small proportion of the dyestuff, in spite of prolonged boiling. In these cases a short steaming is generally found to be effective in overcoming the difficulty. In some cases the peculiar action of steam on wool may be a drawback.

WOOL FAT, *Suint.* Unwashed sheep's wool has the following composition :—12 to 23 per cent. water, 31 to 43 per cent. wool fibre, 3 to 23 per cent. dirt, 28 to 42 per cent. "yolk."

The "yolk" is a mixture of potassium soaps and fatty matters, cholesterol, iso-cholesterol, and homologues and ethers of the same, together with waxy matters, particularly ceryl cerotate.

Wool fat is removed from the fibre by means of volatile solvents or dilute solutions of soda ash. The extraction by means of volatile solvents has not been extensively carried out in England.

If an acid be added to the waste scouring liquor, the soap occurring naturally in the yolk will be decomposed, and fatty acids will be liberated, which, together with the remainder of the fatty and waxy matters present, rise to the surface. As wool fat is insoluble in water, its removal from the aqueous solution is easily effected by heating the mixture with steam before separating the acid liquid. The residual fatty mass is capable of absorbing a considerable amount of water, a fact which is taken advantage of in the preparation of ointments, &c., purified wool fat termed *lanoline* being largely used for this purpose.

Wool fat cannot be saponified by aqueous caustic alkalies.

Purified wool fat has a pale yellow colour and a slight odour. The crude product is brown and has a strong disagreeable smell.

Recovered Fat, *Yorkshire grease.* When an acid acts on a solution of soap, a fatty acid is liberated and an alkaline salt goes into solution. If potassium oleate, which is the chief constituent of an olive oil potash soap, be treated with sulphuric acid, oleic acid rises to the surface and potassium sulphate remains dissolved in the aqueous liquid.

$$2KC_{18}H_{33}O_2 + H_2SO_4$$
$$= K_2SO_4 + 2HC_{18}H_{33}O_2.$$
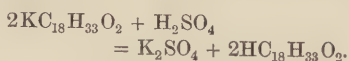
In the washing of wool by means of soap, the waste scouring liquors contain the soap originally used (now partly existing as insoluble calcium soaps), together with the potash soaps naturally present in the wool, and the waxy and fatty matters extracted by the detergent action of the soap.

On treating these waste liquors in wooden tanks with a slight excess of sulphuric acid the soaps are decomposed, as shown in the above equation, and when steam is blown through the mass the fatty and waxy compounds rise to the surface with the liberated fatty acids. After standing for some time the aqueous liquid (containing alkaline sulphates, a small amount of sulphuric acid and any glycerin which may have been present in the soap) is run off. The "magma," as the fatty mixture is termed, is collected and drained on filters made of coarse cocoa-nut matting. It is then transferred to canvas bags and subjected to pressure, first cold and later with the application of steam. The mixture of grease and water flows into a tank. The pressed residue in the canvas-bags still contains about 15 per cent. of grease, which is sometimes extracted by means of carbon bisulphide.

The aqueous emulsion of fat which has been obtained as above is purified by boiling with dilute sulphuric acid. The mixture is allowed to stand and then separated from the water. On cooling it solidifies to a soft brown mass, having a rather unpleasant odour. If necessary it may be bleached by means of a solution of potassium bichromate and sulphuric acid.

Sometimes the product is used in the manufacture of coarse soaps, and sometimes it is distilled for the separation of oleine (liquid constituents) and stearin (solid compounds).

Recovered grease consists essentially of free fatty acids, glycerides (neutral oils), and cholesteroid bodies. The composition, however, varies considerably according to the kind of wool operated upon and the soap used. If the product is from greasy wool, it will contain a high percentage of wool fat and consequently much unsaponifiable matter. If the wool contain but little grease, the recovered fat will consist chiefly of fatty acids derived from the soap. In some cases

the wool is steeped in water previous to scouring, by which means much of the "yolk" and potash salts are removed. In this case the soapy liquors yield a smaller amount of recovered fat, but it is of a superior quality.

Waste soap liquor obtained from the cleansing of materials which have previously been oiled will yield greases containing these substances in addition to the products obtained from the soap.

The following figures show the percentage of saponifiable and unsaponifiable matter in a few samples of recovered grease from wool scouring :—

Unsaponifiable,	25·5	35	42·5	8·5	15·6
Saponifiable,	74·5	65	57·5	91·5	84·4

When large quantities of alkaline carbonates are used in scouring, the value of the recovered fat may be less than the cost of production. The extent to which waste scouring liquors vary in composition is shown by the following partial analyses. All the four samples were obtained from the washing of raw wool :—

In 100 Parts.	1.	2.	3.	4.
Water, ...	99·38	97·10	96·50	97·80
Mineral matter, ...	0·15	1·05	1·30	0·60
Oil or grease, ...	0·27	1·20	1·52	1·36
Other organic matter (by difference), .	0·20	0·65	0·68	0·24
	100·00	100·00	100·00	100·00
Lbs. of pure sulphuric acid required to neutralise 1000 gallons, . . .	7	14	44	22
Lbs. of recovered fat per 1000 gallons, .	27	120	152	136

Recovered grease from the scouring of wool does not contain hydrocarbon oil as a normal constituent, but this is occasionally present, having been added either purposely or accidentally. When the grease is distilled, as it is for many purposes, the product will contain hydrocarbon oils, formed by the partial decomposition of fatty acids.

After wool has been washed it is treated with a certain amount of oil (usually Gallipoli olive oil) to facilitate the carding operation. The wool, in the form of sliver, is subsequently washed with soap in what is known as a back-washing machine. In most works the waste "suds" from this operation are mixed with the waste liquors obtained in washing the raw wool. It is preferable, however, to treat the waste liquor from the back-washing machines separately, since the recovered fatty matter, which contains very little unsaponifiable matter, is much more valuable than the common brown grease.

The waste liquors from yarn scouring (especially worsted yarn) also yield a superior quality of recovered fat, consisting, as a rule, only of the fatty acids derived from the soap and vegetable oils.

WOOL BLACK (Ber.) (B.). An azo dye.

Amidoazobenzene disul- — p. tolyl β-naph-
    phonic acid   thylamine.

1885. Blue-black powder. Aqueous solution, violet. Concentrated H_2SO_4, blue solution ; on dilution, brown precipitate.

Application.—An acid colour. Dyes wool violet-black from an acid bath.

WOOL BLACK B, 2 B, 3 B, 6 B, P, S G (D.). Mark 3 B. Blue-black powder. Aqueous solution, reddish-blue ; alcoholic solution, blue. Concentrated H_2SO_4, dull bluish-green ; on dilution becomes violet.

Application.—Acid dyes for wool.

WOOL BLACK 4 B, 6 B (Ber.). Mark 6 B. Black powder. Aqueous solution, reddish-blue ; alcoholic solution, dull blue. Concentrated H_2SO_4, bright blue ; on dilution, blue precipitate, which re-dissolves on further dilution.

Application.—Acid dyes for wool.

WOOL BLUE S (B.) (S.C.I.). Blue powder. Aqueous and alcoholic solutions, bright blue. Concentrated H_2SO_4, yellow solution ; on dilution, olive-green, then bright blue.

Application.—An acid colour. Dyes wool bright blue from an acid bath.

WOOL GRAY B, G, R (M.) 1890. Black powders, soluble in water. Concentrated H_2SO_4 gives with B and G yellow-brown and with R yellowish-brown solutions which precipitate on dilution.

Application.—Acid colours. Dye wool or silk bluish-, yellowish-, and reddish-grey shades from acid baths.

WOOL GREEN S (B.) (S.C.I.). *Sodium salt of tetramethyl diamidodiphenyl β-oxy-naphthol carbinol sulphonic acid.* 1883. Brown powder with coppery lustre. Soluble in water or alcohol with greenish-blue colour. Concentrated H_2SO_4, brownish-violet solution ; on dilution becomes yellowish green.

Application.—An acid colour. Dyes *wool* or *silk* green.

WOOL RED EXTRA (K.) *v.* AMARANTH.

WOOL SCARLET R (Sch.). An azo dye.

Xylidine — α-naphthol disulphonic acid.

1885. Brownish-red powder. Aqueous solution, yellowish-red. Concentrated H_2SO_4, cherry-red solution ; on dilution becomes redder.

Application.—An acid colour. Dyes *wool* or *silk* scarlet-red.

WOOL VIOLET S (B.). An azo compound.

Dinitraniline — Diethyl m-sulphanilic acid.

1894. Black powder, soluble in water or alcohol with a red-violet colour. Concentrated H_2SO_4, scarlet-red solution ; on dilution, orange-red.

Application.—An acid colour. Dyes *wool* reddish-violet from an acid bath.

WOOL YELLOW (B.) *v.* FUSTINE.

X

XANTHAURINE (G.). An acid yellow dye.

XANTHINE *v.* MADDER.

XANTHINE (P.) (D. & H.) (L.) *v.* PHOSPHINE.

XYLIDINE, $C_6H_3(CH_3)_2NH_2$. The commercial article is a mixture of isomeric compounds. (*v.* ANILINE.)

XYLIDINE ORANGE *v.* BRILLIANT ORANGE R.

XYLIDINE RED *v.* PONCEAU 2 R.

XYLIDINE SCARLET *v.* PONCEAU 2 R.

XYLONITE *v.* COTTON (ACTION OF NITRIC ACID).

Y

YELLOW CORALLIN *v.* AURINE.

YELLOW FAST TO SOAP (O.). An azo dye.

M-amidobenzoic acid — Diphenylamine.

1884. Brown paste, almost insoluble in water. Concentrated H_2SO_4, violet solution ; on dilution, magenta-red.

Application.—A mordant dye, used in printing with chrome mordant.

YELLOW PRUSSIATE OF POTASH *v.* POTASSIUM FERROCYANIDE.

YELLOW T (S.C.I.) *v.* RESORCIN YELLOW.

YELLOW W (By.) *v.* FAST YELLOW (B.).

YELLOW WALLFLOWERS and WHITE HAWTHORN BLOSSOM. Both contain yellow colouring matters, which may be applied in conjunction with alum mordant.

A. G. Perkin[*] has recently shown that the latter contains *quercetin* itself, while wall-flowers contain a *methoxy-quercetin.*

YELLOW WOOD *v.* FUSTIC (OLD).

YELLOW W R (S.C.I.) *v.* BRILLIANT YELLOW S.

YOLK *v.* WOOL.

YORKSHIRE GREASE *v.* WOOL (RECOVERED FAT).

YOUNG FUSTIC *v.* FUSTIC (YOUNG).

Z

ZAMBESI BLACK B, B R, D, F, R (Ber.). Mark B. Greyish-black powder. Aqueous solution, bright blue ; alcoholic solution, reddish-blue. Concentrated H_2SO_4, bright blue ; on dilution, becomes violet.

Application.—Direct cotton colours, diazotised and developed with β-naphthol.

ZAMBESI BLUE B X, B, R X, R (Ber.). Mark B X. Black powder. Aqueous solution, violet ; alcoholic solution, reddish-blue. Concentrated H_2SO_4, bright blue ; unchanged on dilution.

Application.—Direct cotton colours. Dyed either direct or diazotised and developed.

ZAMBESI BROWN G, 2 G (Ber.) Mark G. Violet-black powder. Aqueous solution, bluish-red ; alcoholic solution, dull bluish-red. Concentrated H_2SO_4, bright blue solution ; on dilution, becomes bluish-red.

Application.—Direct cotton colours. As direct dyes they produce dull purplish-browns, but when diazotised and developed yellowish (G G) and dark (G) browns.

ZAMBESI GREY B (Ber.) Greyish-black powder. Aqueous solution, dull blue ; slightly soluble in alcohol, with a dull bluish-red solution. H_2SO_4, bright blue solution ; on dilution, becomes reddish-blue.

Application.—A direct cotton colour. Dyes unmordanted cotton or wool, bluish-grey shade ; on diazotising and developing shade is changed to (β-naphthol) slate shade (resorcin) greenish-grey ; (toluylene diamine) olive-grey ; (amido naphthol ether) greyish-purple.

ZINALIN. An obsolete nitro compound.

ZINC, Zn = 65. Zinc occurs in combination with sulphnr as *zinc blende* (Zn S), and combined with carbon dioxide as *calamine* (Zn CO_3). The metal is extracted from its ores by calcination or roasting, the oxide thus formed being then reduced by heating with ground coal in a retort. The metal volatilises, and is condensed in suitable

[*] *Trans. Chem. Soc.*, 1894, p. 1566.

receivers. It is afterwards purified by melting.

Properties.—Commercial zinc dust obtained from the distillation process contains more or less zinc oxide, iron, and cadmium. It is used as a reducing agent in either alkaline or acid solution. It is also employed in the preparation of indigo vats.

Zinc has a bluish-white colour. Although brittle at the ordinary temperature it can be rolled into sheets at 125° C. At 433° C. zinc melts, and at a bright red heat volatilises and takes fire, burning with a greenish-white flame, with formation of white zinc oxide.

The specific gravity of zinc is 7, and the metal when fractured has a crystalline structure. It tarnishes in moist air, but when pure, water even at 100° C. has no effect on it. Commercial zinc is attacked by boiling water, hydrogen being evolved.

Zinc is dissolved by caustic potash and soda as well as by dilute acids. Under the name "galvanised iron" it is used as a covering for sheets of iron, the latter being merely dipped in the molten zinc.

Brass and a number of other useful alloys contain zinc.

The salts of zinc are soluble in water or in acids, and are colourless. The neutral salts which are soluble in water redden litmus, have a metallic taste, and are poisonous.

Analysis of Zinc Powder.—*Zinc dust, zinc preparation, or zinc powder* contains, in addition to metallic zinc, variable quantities of zinc oxide, iron, cadmium, silica, &c. As it is largely used as a reducing agent in the preparation of indigo vats, its value for such purposes depends entirely upon the amount of metallic zinc present.

Drewson* determines the percentage of zinc by its action upon an excess of a standard solution of potassium bichromate. For this purpose 0·661 grm. of the sample (this amount of pure zinc reduces 1 grm. of $K_2Cr_2O_7$) is mixed with 80 c.c. of a solution containing 25 grms. of potassium bichromate per litre and 10 c.c. of dilute sulphuric acid. The same amount of dilute acid is added after fifteen minutes, and the addition repeated a third time, the liquid being stirred from time to time. 10 c.c. of concentrated sulphuric acid, diluted with its own volume of water, are now added, followed by an excess (about 10 grms.) of *pure* granulated ferrous ammonium sulphate. If, after well stirring, a drop of the solution does not produce a blue colour when brought in contact with a drop of potassium ferricyanide, a further weighed amount of the ferrous ammonium sulphate must be added. The excess of ferrous salt is then determined by the standard solution of bichromate. The amount of potassium bichromate reduced by 0·661 grm. of the

* *Journ. Soc. Chem. Ind.*, 1887, p. 147.

sample, multiplied by 100, gives the percentage of metallic zinc present. Any metallic iron present will, of course, also be included.

Example.—0·661 grm. with 80 c.c. of a solution of potassium bichromate (25 grms. of $K_2Cr_2O_7$ per litre) were subsequently treated with 10 grms. of ferrous ammonium sulphate. 6·1 c.c. of the same bichromate solution were required to oxidise the excess of ferrous iron. (1 grm. of ferrous ammonium sulphate = 0·1255 grm. $K_2Cr_2O_7$.)

0·025 × 86·1 = 2·1525 = total $K_2Cr_2O_7$.
0·1255 × 10 = 1·2550 = $K_2Cr_2O_7$ used by
——— $Fe(NH_4)_2(SO_4)_2.6H_2O$
·8975 = $K_2Cr_2O_7$ reduced
by zinc.

∴ 0·8975 × 100 = 89·95 per cent. of zinc in the sample.

Instead of adding such a large quantity of ferrous ammonium sulphate, the operation may be modified by diluting the solution containing the excess of potassium bichromate to a given bulk, and estimating the amount of $K_2Cr_2O_7$ still present, as given under BICHROMATES (*q.v.*).

Liebschütz* takes 1 grm. of the sample, removes the iron by means of a magnet, and moistens the powder with alcohol in a beaker, stirs with a small platinum rod, and covers it with a warm neutral solution of 5 grms. of copper sulphate. After digesting for some time, the mixture is acidified with a few drops of dilute sulphuric acid. After the copper is deposited the liquid is poured through a small filter, and the deposit is washed by decantation with warm water until copper can no longer be detected in the filtrate by means of potassium ferrocyanide. The copper, together with the ash of the filter, is dissolved in nitric acid, any lead here present is removed, the solution is made up to a known volume, and the copper is determined volumetrically in an aliquot part thereof by means of titration with a standard solution of potassium cyanide. The weight of copper found, multiplied by 1·032, equals the amount of zinc in the sample taken.

F. Weil† employs a standard solution of copper chloride, and after the action of the weighed sample of zinc, estimates the residual copper in solution by stannous chloride. A solution of copper chloride containing 10 grms. of Cu per litre is prepared by dissolving 12·519 grms. of pure copper oxide (obtained by ignition of the nitrate) in a slight excess of hydrochloric acid and diluting to a litre. 50 c.c. (= 0·5 grm. of Cu) are introduced into a porcelain or platinum capsule, and dilute ammonia carefully added until the liquid

* *Journ. Amer. Chem. Soc.*, vol. vii., p. 136
† *Chemical News*, vol. liv., p. 314.

24

becomes slightly opalescent. A weighed amount (0·4 grm.) of the sample of zinc powder is now added, and a platinum wire coiled at the lower end in the form of a spiral is used to stir the mixture occasionally. When the operation is complete (known by no deposit being formed on a clean platinum wire when stirred up in the mixture) a few drops of acetic acid are added, and the liquid decanted into a graduated 200 c.c. flask. The capsule and the precipitated copper are well washed with water and the whole diluted to the 200 c.c. mark and well mixed. After allowing any insoluble matter to subside, 20 c.c. of the clear solution are put into a small flask, mixed with 40 c.c. of pure hydrochloric acid, and titrated at the boil until completely decolorised, with a solution of stannous chloride which has been standardised by the original copper solution. Deducting the copper found in solution from 0·5 grm., the weight of copper precipitated by the zinc in the sample is obtained. The weight multiplied by 1·032, as given above, represents the amount of metallic zinc in the portion taken for analysis.

The percentage of metallic zinc may also be determined from the volume of hydrogen evolved when a weighed amount of zinc powder is treated with dilute sulphuric or hydrochloric acid.

F. Meyer * describes a special apparatus for the analysis of zinc powder by the last-mentioned method.

ZINC ACETATE, $Zn(C_2H_3O_2)_2 + 2H_2O$. Zinc acetate occurs in the form of white crystals, which easily dissolve in water. Its use has been suggested as a substitute for tartar emetic for fixing tannic acid. A solution of 5 parts of sodium acetate and 10 parts of zinc sulphate in 1000 parts of water may be used for this purpose.

ZINC CARBONATE, $ZnCO_3$. Carbonate of zinc occurs native as *calamine*. It may be prepared by mixing zinc sulphate solution with sodium bicarbonate. If the normal carbonate (Na_2CO_3) be used, basic zinc carbonates are precipitated.

ZINC CHLORIDE, $ZnCl_2$.

Preparation.—Zinc chloride may be obtained in the anhydrous state by the distillation of zinc sulphate and calcium chloride. It is also formed in solution by treating zinc oxide suspended in calcium chloride solution with carbon dioxide, whereby calcium carbonate is precipitated. Zinc chloride is generally manufactured as follows :— Sheet zinc, carefully sorted so as to contain no galvanised iron, is dissolved in stone or wooden vessels. If stone ones be used, iron rods should be avoided, as a spark caused by friction might cause an explosion of the hydrogen liberated during the reaction. The

* *Journ. Soc. Chem. Ind.*, 1894, p. 841.

vessel must be fitted with a wooden chimney by means of which the gases can escape. If the hydrochloric acid is not too weak a solution will be obtained of from 98° to 110° Tw., which is only slightly acid and can often be used directly.

This solution contains also other metals, chiefly iron. If a pure white chloride of zinc is wanted, the iron and manganese must be removed by neutralising with soda, heating to about 45° C., and adding chloride of lime in solution. The iron and manganese are then precipitated ; they settle quickly, and the clear solution may be filtered or decanted off, and evaporated down in enamelled vessels. These should have a capacity of about 100 to 200 litres and be heated direct by fire. The evaporation is continued until the temperature rises to about 240° C., a little chlorate of potash is added as the liquor will have become somewhat yellow again. Some hydrochloric acid (free from iron) is very carefully added by means of a long tube-funnel, having the end in the hot solution, in order to hinder the formation of basic salts at the close of the drying down. The zinc chloride is allowed to cool in the enamelled vessel, stirring slowly, and the crystalline mass packed, whilst still warm, in tins, which are pasted down with paper so as to hermetically close them. Unscrupulous makers sometimes add 25 per cent. common salt before crystallisation, which has this advantage that one need not evaporate higher than 190° C., as the salt attracts water and the zinc chloride crystallises sooner. It is therefore advisable to determine the amount of *zinc* in the commercial article.

Properties.—Zinc chloride forms a white mass, which melts at about 110° C. and distils at 680° C. without decomposition. It quickly takes up moisture from the air, and removes the elements of water from organic substances. It is easily soluble in water, the aqueous solution undergoing decomposition on boiling, hydrochloric acid being evolved, and a basic salt, zinc oxychloride, $ZnCl(OH)$, being produced. The latter salt can also be obtained by boiling zinc chloride with zinc oxide. An addition of water to the basic salt causes the precipitation of mixtures of zinc oxychloride and zinc hydrate.

Zinc chloride has a strong caustic action, and is used in surgery ; the solution is also employed as a preservative in the arts, for deodorising, &c. On boiling a solution of zinc chloride (1·7 sp. gr.) with excess of zinc oxide an oxychloride is formed which dissolves silk. Advantage is taken of this property, the solution being made use of in the analysis of textile fabrics.

Zinc chloride is used as a constituent of the size for cotton goods, its action being hygroscopic and antiseptic.

Analysis.—The commercial solution containing about 20 per cent. of zinc chloride often contains oxide of zinc dissolved in it. This oxide is objectionable, and as the zinc chloride only is required, the oxide should be removed by adding water and filtering, and determining the zinc chloride in the filtrate. The solution is then nearly neutralised, mixed with excess of sodium acetate and a little acetic acid, heated to boiling, and a brisk current of hydrogen sulphide passed in for half an hour. The precipitate of zinc sulphide is filtered and washed. It is then dissolved in hydrochloric acid, and sodium carbonate added in slight excess. The carbonate of zinc is filtered, washed, dried, and ignited, and the resulting oxide of zinc (ZnO) weighed.

ZINC CHROMATE, Zn CrO₄. *Zinc Yellow.*
Chromate of zinc is formed by adding a hot neutral solution of zinc sulphate to potassium chromate. It is a beautiful yellow pigment.

ZINC FERROCYANIDE is used as a fixing agent for aniline colours and aniline black.

ZINC HYDROXIDE, Zn(OH)₂. On the addition of alkalies to zinc salts, zinc hydrate is precipitated as a white amorphous powder. Caustic alkalies or dilute acids dissolve it. On heating, the hydroxide is decomposed into zinc oxide and water.

The compounds formed by the solution of zinc hydrate in caustic alkalies are termed *zincates.*

$$Zn(OH)_2 + 2NaOH = Zn(ONa)_2 + 2H_2O.$$
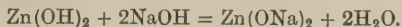
Zincates of aluminium and magnesium may be formed by treating salts of these metals with sodium zincate.

$$3Zn(ONa)_2 + Al_2(SO_4)_3$$
$$= Al_2(ZnO)_3 + 3Na_2SO_4.$$
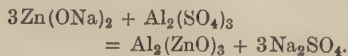
Compound mordants can be obtained by passing the goods through a solution of aluminium, chromium, or magnesium, and then through sodium zincate. Prudhomme[*] has made an exhaustive research on these compound mordants.

ZINC LACTATE, Zn(C₃H₅O₃)₂ + 3H₂O.
Preparation.—Kiliani[†] gives the following method :—500 grms. cane sugar are dissolved in 250 c.c. water and 10 c.c. sulphuric acid (3 acid : 4 water) added, and the whole warmed to 50° C. for two hours. The solution is cooled and 400 c.c. caustic soda solution (1 : 1) added, the mixture being kept cool. The *exact* amount of acid necessary, of the same strength as above, is then added. A crystal of Glauber's salt is added, to start the crystallisation of the sodium sulphate, and the cold solution left for twenty-four hours.

[*] *Journ. Soc. Dyers and Col.,* 1891, p. 133.
[†] *Berichte d. d. Chem. Ges.,* vol. xv., p. 699.

The mass is then extracted with 93 per cent. alcohol, filtered with the aid of a pump, and half of the filtrate neutralised with zinc carbonate on the water-bath. The second half of the filtrate is then added and the whole left to crystallise. Zinc lactate crystallises from the solution and is purified by re-crystallisation.

Properties. — Zinc lactate crystallises in colourless rhombic prisms. On drying at 100° C. its water of crystallisation is driven off. It is soluble in 60 parts of water at 15° C., and in 6 parts at the boiling temperature. The aqueous solution has a bitter taste.

Clarke and Boehrininger[*] have patented a process for employing zinc lactate in place of antimony and tannin for fixing basic colours on cotton.

Cotton mordanted with zinc lactate is also capable of fixing mordant colouring matters.

ZINC NITRATE, Zn(NO₃)₂ + 6H₂O. Zinc nitrate forms deliquescent crystals. At 100° C. it is decomposed, water and nitric acid being given off and a basic salt formed. At a red heat zinc oxide is formed.

It is made by treating a solution of lead nitrate with zinc sulphate, or by dissolving zinc in nitric acid. Boiling with zinc oxide will effect the removal of iron from the solution of zinc nitrate. Printers use zinc nitrate as an addition to the thickening, to prevent premature decomposition. It is sometimes added to colours in woollen printing on account of its hygroscopicity.

ZINC OXIDE, ZnO. Oxide of zinc is formed as a voluminous white mass by the combustion of zinc in air. The nitrate and the carbonate of zinc are decomposed on ignition, leaving oxide of zinc as a dense white mass. Zinc oxide on heating becomes temporarily of a yellow colour. It is used as a pigment under the name *zinc white.* Sulphuretted hydrogen does not turn this pigment black.

ZINC SULPHATE, Zn SO₄ + 7H₂O.
Preparation.—When zinc is dissolved in sulphuric acid, crystals of sulphate of zinc separate from the solution. It is prepared on the large scale by gently roasting zinc blende (Zn S) and extracting the zinc sulphate thus formed with water.

Properties.—At the ordinary temperature 100 parts of water dissolve about 150 parts of the hydrated salt. The solution has an acid reaction and is poisonous. The salt is efflorescent in the air, and on heating to 100° C. loses 6 molecules of water.

Zinc sulphate is used for weighting cotton goods, in calico printing, and sometimes in dyeing wool with basic colours.

[*] *Journ. Soc. Dyers and Col.,* 1896, p. 222.

SYMBOLS AND ATOMIC WEIGHTS OF THE COMMONEST ELEMENTS.

	Symbols.	Weights.
Aluminium,	Al	27·1
Antimony,	Sb	120
Arsenic,	As	75
Barium,	Ba	137
Bismuth,	Bi	208
Bromine,	Br	80
Cadmium,	Cd	112
Calcium,	Ca	40
Carbon,	C	12
Chlorine,	Cl	35·5
Chromium,	Cr	52·5
Cobalt,	Co	59
Copper,	Cu	63·2
Hydrogen,	H	1
Iodine,	I	127
Iron,	Fe	56
Lead,	Pb	206·5
Magnesium,	Mg	24
Manganese,	Mn	55
Mercury,	Hg	200
Nickel,	Ni	59
Nitrogen,	N	14
Oxygen,	O	16
Phosphorus,	P	31
Platinum,	Pt	194·5
Potassium,	K	39
Silver,	Ag	107·5
Sodium,	Na	23
Strontium,	Sr	87
Sulphur,	S	32
Tin,	Sn	117·5
Tungsten,	W	184
Uranium,	Ur	239
Vanadium,	Va	51
Zinc,	Zn	65

THE END.

Lay Page 29   Bleach
        5 np

Page 303   Sodium Dioxide ⎫ Bleach
        "   Peroxide   ⎭

Zinc Acetate Fixer 310

Soap formula 283   (Waterproofs   355